

SYNTHESES IN THE
4:5-METHYLENEPHENANTHRENE SERIES

by

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THESIS submitted for the degree of
DOCTOR of PHILOSOPHY

September, 1954.

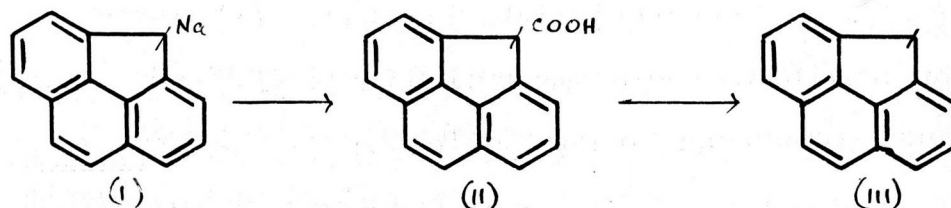
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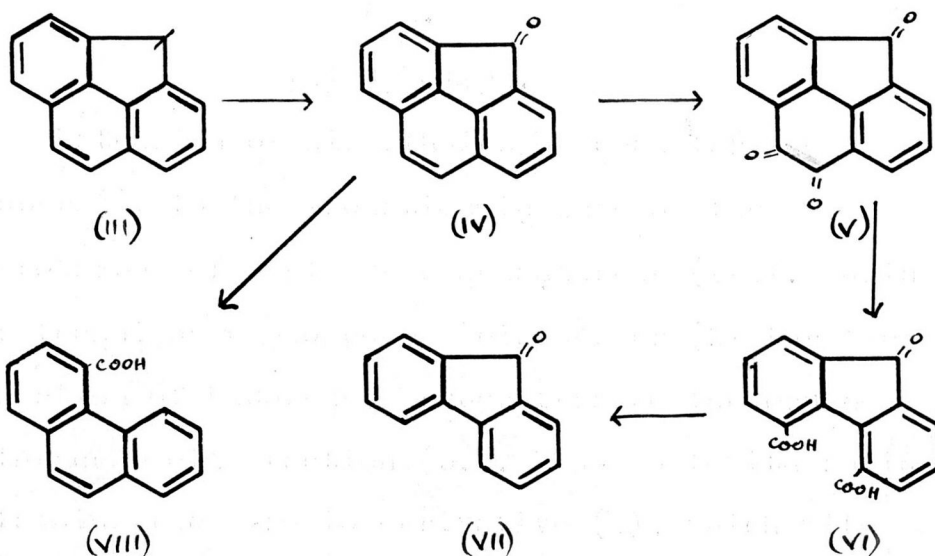
INTRODUCTION.

Extension of his studies on coal tar led Kruber (1) to the isolation in 1934 of the hydrocarbon 4:5-methylenephenanthrene (III). Using the technique employed by Weissgerber (2) for the isolation of fluorene, Kruber treated the crude anthracene oil fraction (b.p. 350-360°) with sodium, obtaining the α -sodio derivative (I), which with carbon dioxide gave the sodium salt of α -carboxy-4:5-methylenephenanthrene (II). This on decarboxylation yielded the hydrocarbon itself.

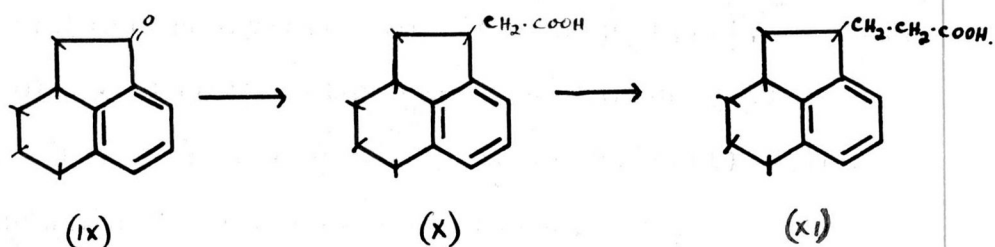


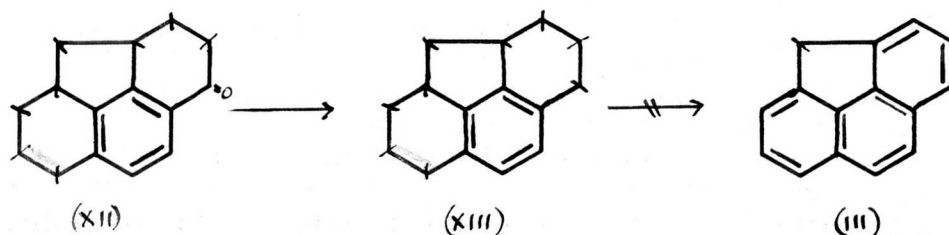
The constitution of the hydrocarbon was established by oxidative methods which showed the presence of both the fluorene and phenanthrene nuclei. Mild oxidation afforded α -keto-4:5-methylenephenanthrene (IV) which on more vigorous treatment gave first α -keto-4:5-methylene-9:10-phenanthraquinone (V) and then fluorenone-4:5-dicarboxylic acid (VI). The latter was decarboxylated to fluorenone (VII). Alkali fusion of α -keto-4:5-methylenephenanthrene (IV) yielded phenanthrene-4-carboxylic acid (VIII) which gave phenanthrene on decarboxylation.

2.



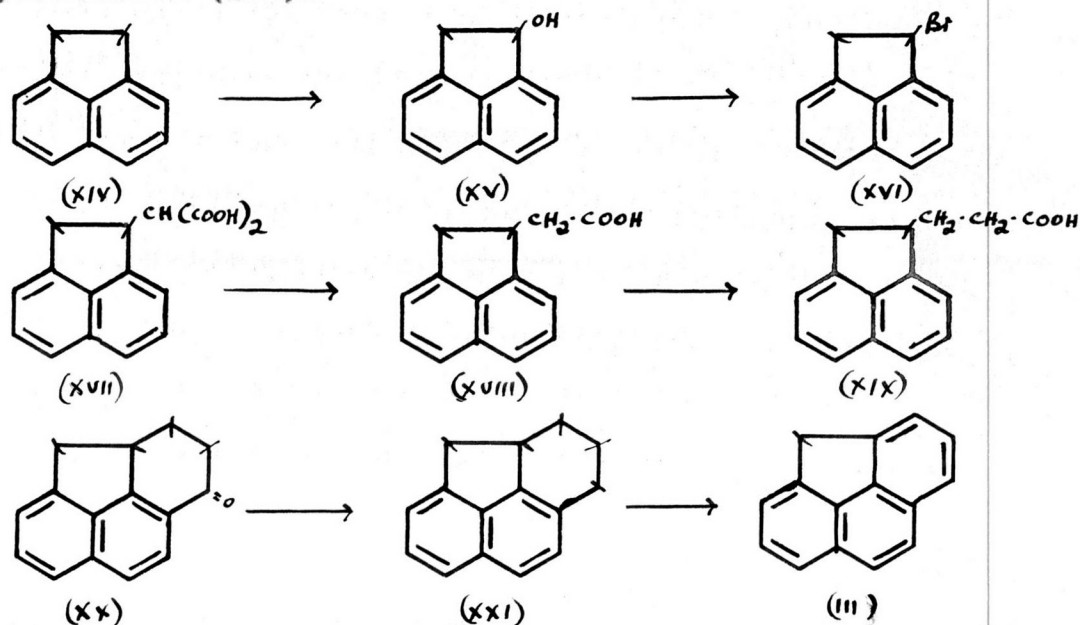
Previously, in 1928, a synthesis of 4:5-methylenepheneanthrene had been attempted by von Braun and Rath (3). The Reformatsky reaction on tetrahydroacenaphthenone (IX) gave a mixture of unsaturated acids, hydrogenation of which afforded tetrahydroacenaphthenyl-1-acetic acid (X). The side chain was lengthened via the alcohol, bromide and cyanide, and the tetrahydroacenaphthenylpropionic acid (XI) obtained on hydrolysis was cyclised to the ketone (XII). Clemmensen reduction gave the octahydro-4:5-methylenepheneanthrene (XIII), but all attempts at dehydrogenation failed. This inability to aromatise the molecule was attributed by von Braun to the steric strain which, he believed, would be introduced into the ring system.



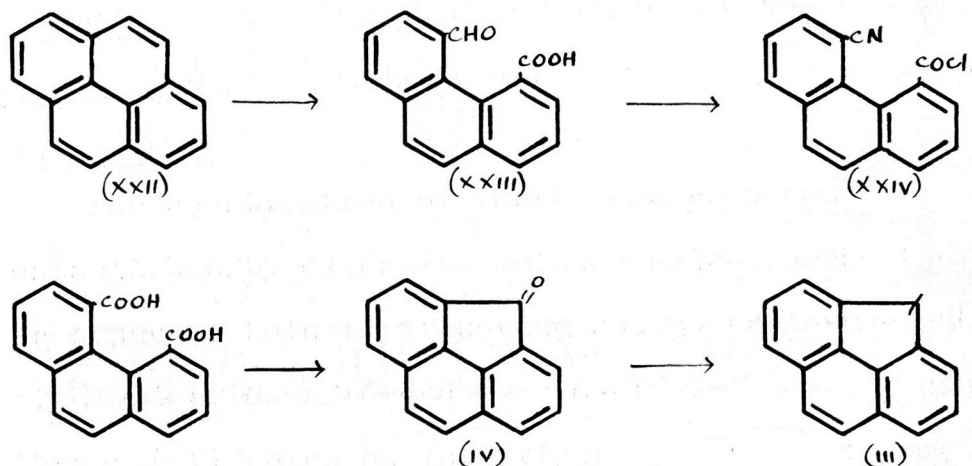


The first successful synthesis of 4:5-methylenepheneanthrene was accomplished by Bachmann and Sheehan (4), thus confirming the structure put forward by Kruber.

Acenaphthene (XIV) was oxidised to acenaphthenol (XV), which was converted into the bromide (XVI) and condensed with sodio-malonic ester. The substituted malonic acid (XVII) so obtained was decarboxylated to acenaphthenyl-1-acetic acid (XVIII). The Arndt-Eistert reaction gave acenaphthenyl-1-propionic acid (XIX) which was cyclised to 1-keto-1:2:3:4-tetrahydro-4:5-methylenepheneanthrene (XX). Reduction to 1:2:3:4-tetrahydro-4:5-methylenepheneanthrene (XXI) followed by dehydrogenation afforded the aromatic hydrocarbon (III).



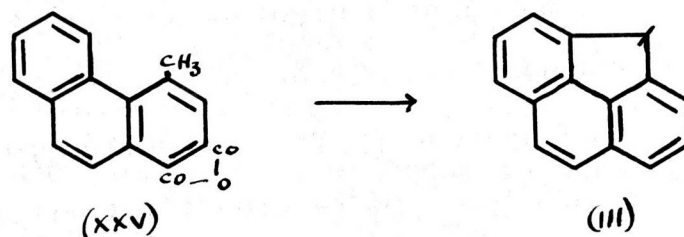
More recently, a synthesis of 4:5-methylenepheneanthrene has been developed by Medenwald (5) which involves the reduction in size of one of the rings in the pyrene molecule. Pyrene (XXII) on ozonisation gave 4-carboxy-5-phenanthraldehyde (XXIII) which was converted into the oxime. Dehydration with thionyl chloride afforded 5-cyanophenanthrene-4-carboxylic acid chloride (XXIV) hydrolysis of which yielded phenanthrene-4:5-dicarboxylic acid. Dry distillation of the barium salt gave α -keto-4:5-methylenepheneanthrene (IV) which was reduced by the Wolff-Kishner method to the hydrocarbon (III).



It is of interest to note that Bergman and Weizmann (6), in studying the Diels Alder reaction on certain vinyl naphthalenes, isolated the anhydride of 4-methylphenanthrene-1:2-dicarboxylic acid (XXV).

5.

Dry distillation of the potassium salt gave a small amount of a mixture of hydrocarbons which yielded a picrate corresponding in melting point to that of 4:5-methylenephenanthrene. No direct comparison with authentic material was made, but the authors suggested that, at the high reaction temperature, cyclodehydrogenation had occurred to give 4:5-methylenephenanthrene (III).



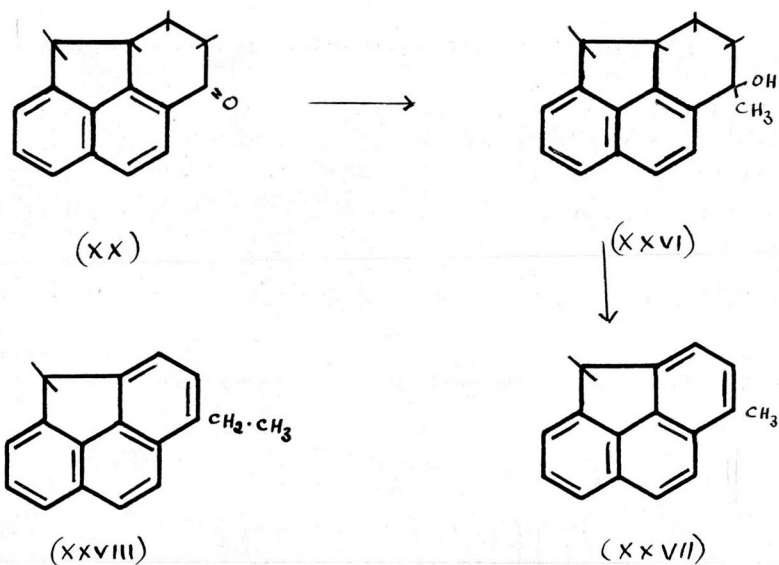
In recent months, Kruber (7) has intimated an improvement in the isolation of 4:5-methylenephenanthrene from coal tar distillates.

Largely due to its inaccessibility, 4:5-methylenephenanthrene has not been intensively studied. (c.f. Reid: Thesis, (Edin.), 1951, and Swan: Thesis, (Edin.), 1952). For example, only three alkyl derivatives are known. These are the 3-methyl, 3-ethyl and 1-ethyl compounds which have all been synthesised by Bachmann and Sheehan (8).

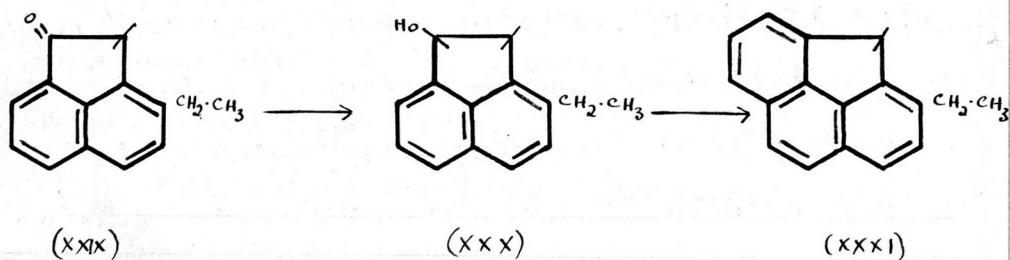
Treatment of 1-keto-1:2:3:4-tetrahydro-4:5-methylenephenanthrene (XX), obtained as an intermediate in the original synthesis, with methylmagnesium bromide gave the carbinol (XXVI) which on dehydration and dehydrogenation, yielded 1-methyl-

4:5-methylenephenanthrene (XXVII).

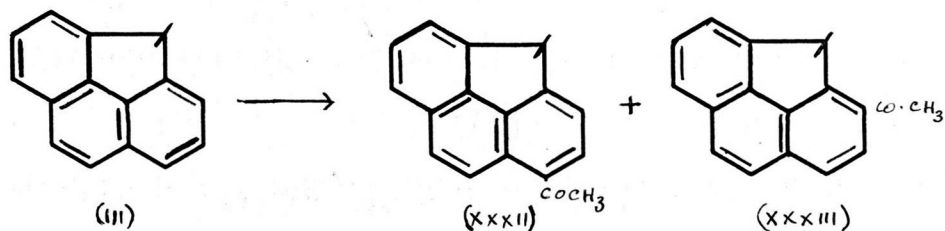
Similarly, treatment with ethylmagnesium bromide gave 1-ethyl-4:5-methylenephenanthrene (XXVIII).



Application of the original synthesis to 3-ethyl-1-acenaphthenol (XXX), obtained by the Meerwein-Pondorff reduction of 3-ethyl-1-acenaphthenone (XXIX), led to 3-ethyl-4:5-methylenephenanthrene (XXXI).

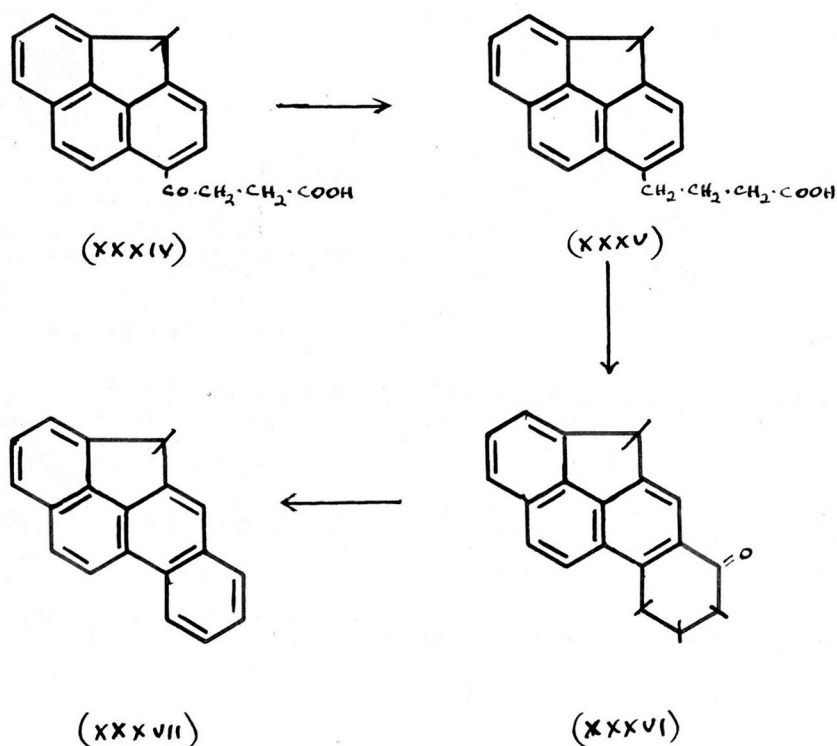


Acetylation of 4:5-methylenephenanthrene with acetyl chloride and aluminium chloride in nitrobenzene, gave a mixture of the 1-acetyl and 3-acetyl derivatives (XXXII, XXXIII). These were reduced to the corresponding ethyl compounds which were shown to be identical with those prepared as above.

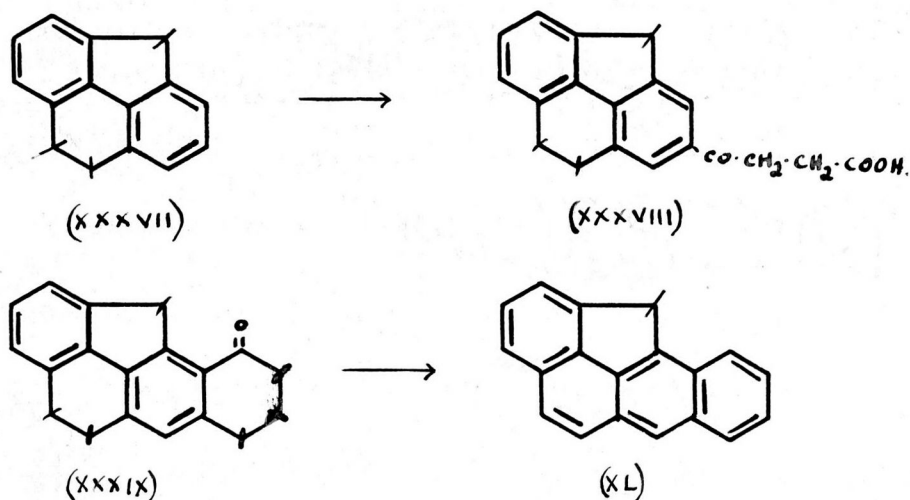


There are several instances where 4:5-methylenepheneanthrene has been utilised as the starting material for the syntheses of higher ring systems.

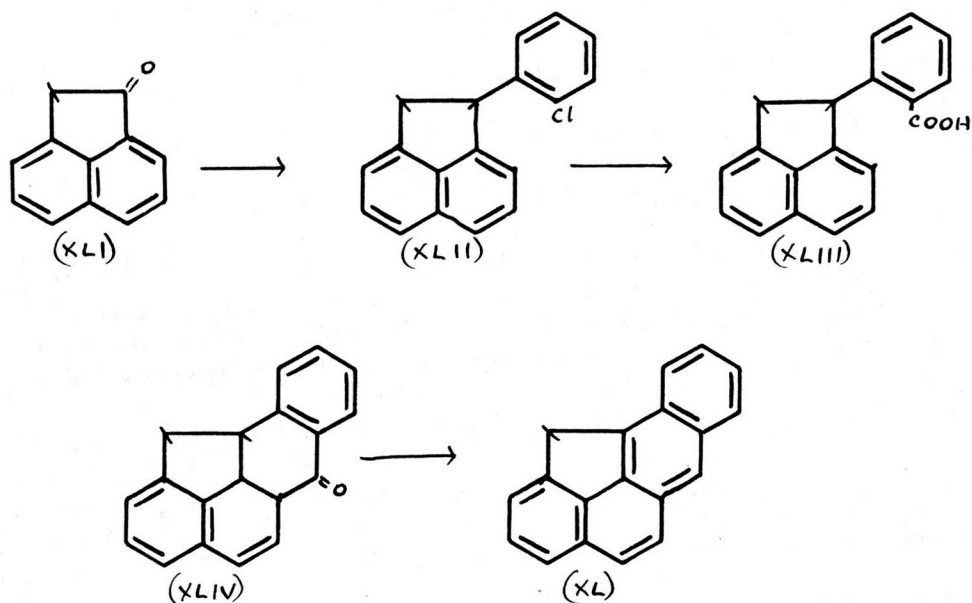
a) Fieser and Cason (9) found that the succinylation of 4:5-methylenepheneanthrene gave a mixture of keto acids from which only one isomer, the 1-keto acid (XXXIV), could be isolated. Ring closure of the reduced acid (XXXV) gave the ketone (XXXVI) which on reduction and dehydrogenation yielded 4:5-methylenechrysene (XXXVII).



b) Catalytic hydrogenation of 4:5-methylene-phenanthrene (9) resulted in saturation of the 9:10-double bond, and succinoylation of the 9:10-dihydro-4:5-methylenepheneanthrene (XXXVII) so obtained gave a homogeneous product. This was shown to be the 2-keto acid (XXXVIII) which on reduction and cyclisation gave the ketone (XXXIX). Reduction of the ketone to the hexahydride followed by dehydrogenation gave 1':9-methylene-1:2-benzanthracene (XL).

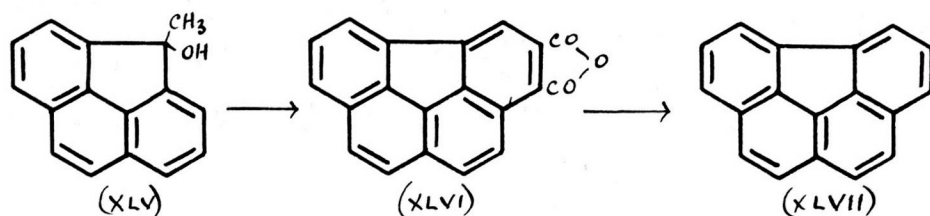


This hydrocarbon was also synthesised by reacting 1-acenaphthenone (XLI) with o-chlorophenyl-magnesium bromide. The carbinol isolated from the Grignard reaction was reduced to o-chlorophenyl-1-acenaphthene (XLII), and the chlorine replaced by a cyano group. Ring closure of the acid (XLIII) obtained on hydrolysis gave the ketone (XLIV) which was reduced and dehydrated to 1':9-methylene-1:2-benzanthracene (XL).

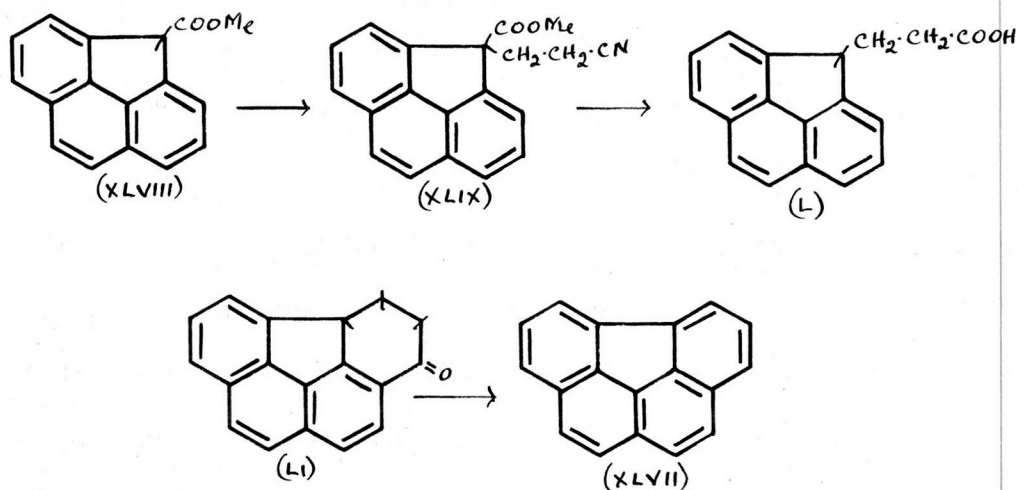


c) The salient feature of the chemistry of 4:5-methylenepheneanthrene is the reactivity of the methylene group, in which the hydrocarbon shows a close resemblance to the chemical behaviour of fluorene. This reactivity has been exploited by Campbell and Reid (10) in the synthesis of 2:13-benzfluoranthene (XLVII) and 2:13-11:12-dibenzfluoranthene (LIII).

Treatment of -keto-4:5-methylenepheneanthrene (IV) with methylmagnesium iodide gave the carbinol (XLV) which with maleic anhydride in acetic anhydride yielded the fully aromatic 2:13-benzfluoranthene-11:12-dicarboxylic anhydride (XLVI). This on decarboxylation gave 2:13-benzfluoranthene (XLVII).

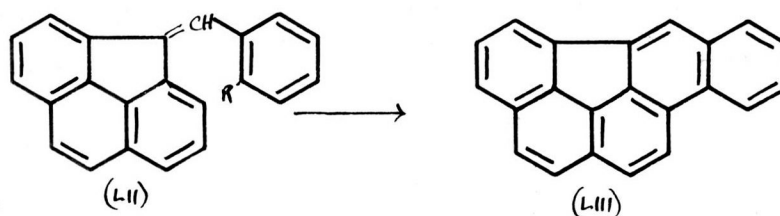


The same authors condensed acrylonitrile with methyl 4:5-methylenephenanthrene- -carboxylate (XLVIII) to give the nitrile (XLIX). Hydrolysis afforded the acid (L) which was cyclised to 12-keto-9:10:11:12-tetrahydro-2:13-benzfluoranthene (LI). Reduction followed by dehydrogenation yielded the hydrocarbon (XLVII).

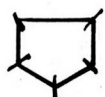


Kruber (7) has isolated from coal tar a hydrocarbon which has been shown to be identical with that synthesised as above.

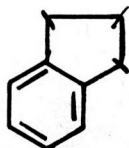
d) Campbell and Reid (10) effected the condensation of 4:5-methylenephenanthrene and o-chloro or o-bromobenzaldehyde, so obtaining the benzal derivatives (LII, R = Cl or Br), which on cyclisation with potassium hydroxide in quinoline afforded 2:13-11:12-dibenzfluoranthene (LIII).



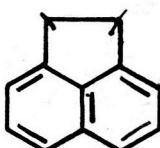
4:5-methylenephenanthrene (III) and 2:13-benzfluoranthene (XLVII) may be regarded as members of the series: cyclopentane (LIV), hydrindene (LV), acenaphthene (XIV),



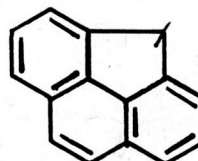
(LIV)



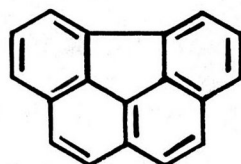
(LV)



(XIV)



(III)



(XLVII)



(LVI)

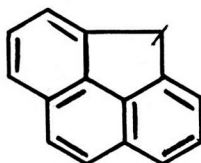
The ultimate member of this series is the hydrocarbon (LVI) which has been named coronindene. This hypothetical substance has not yet been synthesised and indeed, doubts have been raised as to whether such a molecule can exist in view of the abnormal distortions which must be introduced in order to accommodate the structure. In recent months, however, Kruber (7) has isolated from coal tar a yellow substance m.p. 162°, which analyses correctly for the hydrocarbon (LVI) and which, he tentatively suggests, may be coronindene.

OBJECT OF RESEARCH.

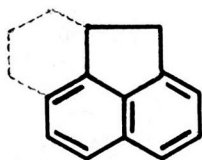
Apart from its intrinsic chemical interest, 4:5-methylenephenanthrene is an important intermediate in the synthesis of higher ring systems, and its preparation in reasonable quantities is highly desirable. It is obtainable by Bachmann's synthesis which, however, requires several months work to complete and furnishes only moderate amounts of material. It was therefore decided to explore the possibilities of synthesising the hydrocarbon by other (preferably shorter) methods.

DISCUSSION OF RESULTS.SECTION A.ATTEMPTED SYNTHESSES OF 4:5-METHYLENEPHENANTHRENE.

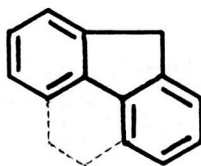
Since 4:5-methylenephenanthrene (III) embodies the structures of acenaphthene (XIV), fluorene (LVII) and phenanthrene (LVIII), these three hydrocarbons represent the possible starting materials for the synthesis of 4:5-methylenephenanthrene, the problem in each case being that of building on a fourth ring.



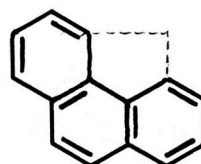
(III)



(XIV)



(LVII)



(LVIII)

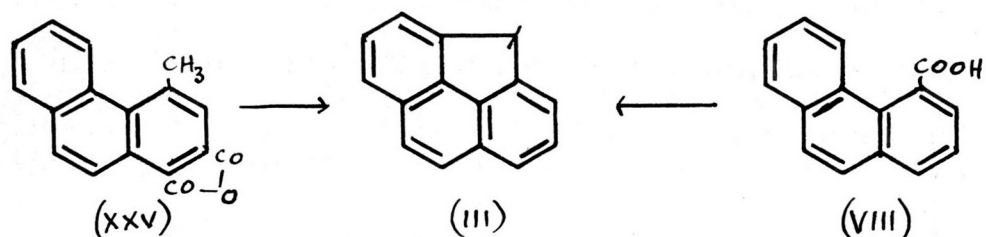
This section has been subdivided on this basis and deals with attempted syntheses of 4:5-methylenephenanthrene from acenaphthene, fluorene and phenanthrene or their derivatives.

SECTION A.

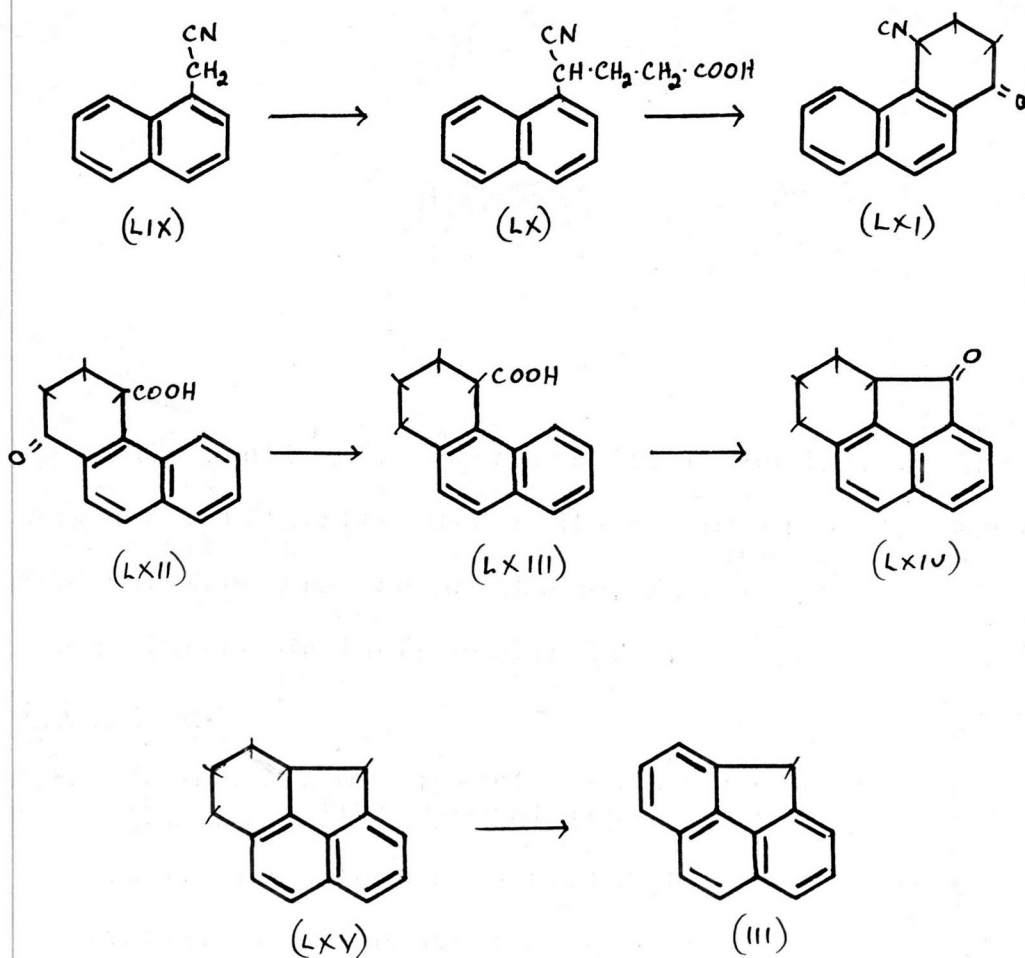
(1) Synthesis of 4:5-Methylenephenanthrene from Phenanthrene.

It is known that a 4-substituted phenanthrene derivative may be converted into 4:5-methylenephenanthrene, e.g. Weizmann (6) claimed that

4:5-methylenephenanthrene (III) was formed in the decarboxylation of 4-methylphenanthrene-1:2-dicarboxylic anhydride (XXV). It therefore seemed possible that a route to the desired hydrocarbon might be found via phenanthrene-4-carboxylic acid (VIII).

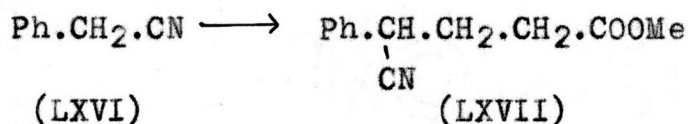


An outline of the proposed scheme is given below.

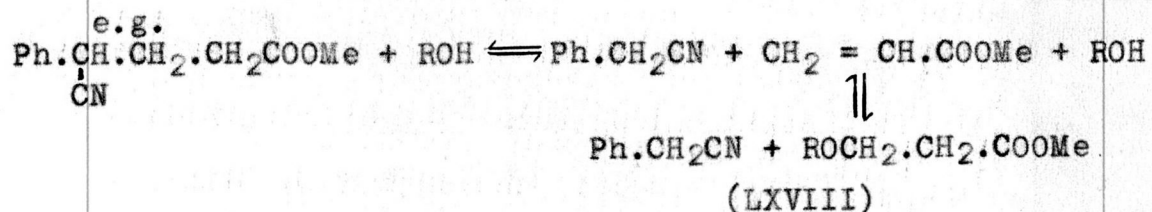


Naphthalene was chloromethylated in the 1-position and converted to 1-naphthylacetonitrile (LIX) by the method of Briggs and Wilson (11).

Before proceeding to the next stage of the synthesis, the Michael condensation of 1-naphthylacetonitrile with methyl acrylate, preliminary experiments were carried out with phenylacetonitrile (LXVI). An attempted condensation with methyl acrylate made in ethoxyethanol containing potassium hydroxide was unsuccessful, but the use of pyridine as solvent and sodium methoxide as catalyst afforded γ -cyano- γ -phenylbutyric ester (LXVII) in 20% yield. The course of the reaction was followed by the temperature rises and colour changes which occurred.



The same condensation, catalysed by sodium methoxide, has been carried out by Koelsch (12) in the absence of any solvent, with an identical yield of the ester (LXVII). He showed that methyl acrylate and acrylonitrile readily react with simple alcohols in the presence of sodium methoxide to form methyl β -alkoxypropionates (LXVIII) or the corresponding nitriles, thus upsetting the equilibrium, which in the Michael reaction mixture is normally displaced to the left.



On the other hand, Tucker (13) has successfully carried out a series of Michael condensations between methyl fluorene-9-carboxylate and unsaturated esters such as methyl acrylate and methyl crotonate. The reactions proceeded readily in methanol in the presence of sodium methoxide. The answer to this anomaly may lie in the relative reactivities of the methylene centres, but in any case, it is probable that in the experiment using ethoxyethanol as solvent, an addition product was formed with the methyl acrylate.

Under the same conditions used for phenylacetonitrile, 1-naphthylaceto nitrile (LIX) reacted with methyl acrylate to give γ -cyano- γ :1-naphthylbutyric acid (LX) in 40% yield. As before, colour and temperature changes indicated the course of the reaction, which required several days for completion. The acid (LX) was isolated via a low melting salt which crystallised from the carbonate washings either spontaneously or on seeding. Ignition of the salt on platinum foil gave a slight residue which when dissolved in a drop of water showed a strongly alkaline reaction. The analysis figures agree with the theoretical values required for the sodium salt

of δ -cyano- δ :1-naphthylbutyric acid (LX) containing three molecules of water of crystallisation to one molecule of salt. The low melting point (58°) can then be interpreted as dissolution of the salt in its own water of crystallisation, and indeed, when the melting point was determined by the capillary tube method, it was observed that the melt boiled on raising the temperature to 105° .

A warm aqueous solution of the salt, on acidification, gave the desired cyano acid which could be converted into the salt again by carbonate extraction of an ethereal solution of the acid. The separation of the salt was utilised in the purification of the acid. Crystallisation of the crude product from benzene or aqueous acetic acid gave material which, under the microscope, was seen to consist of two components which melted at different temperatures. By dissolving in anhydrous benzene and removing traces of water by azeotropic distillation, the formation of hydrates was avoided and a pure product was obtained.

Attempts to cyclise the cyano acid (LX) with stannic chloride in benzene (via the acid chloride) yielded non-ketonic neutral products along with appreciable quantities of impure starting material. Anhydrous aluminium chloride in nitrobenzene, however, gave 1-keto-4-cyano-1:2:3:4-tetrahydro pheanthrene (LXI) in 38% yield. Acid hydrolysis

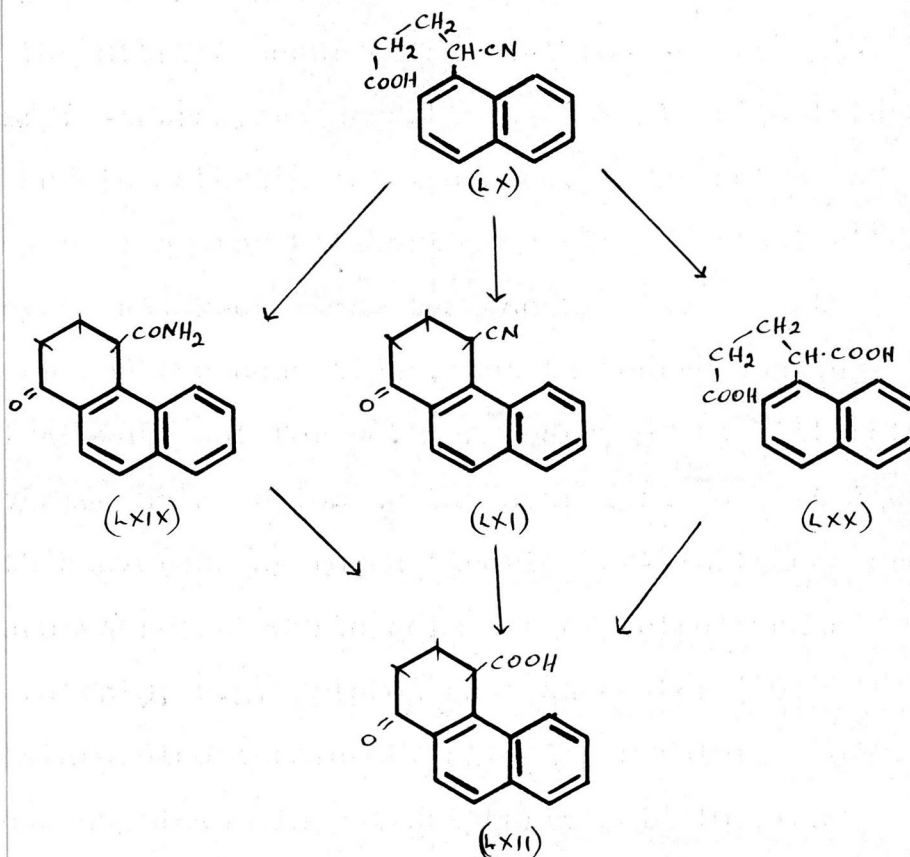
of the keto nitrile afforded a good yield of 1-keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene (LXII), the identity of which was proved by a mixed melting point determination with authentic material prepared by Ansell and Hey (14) in their synthesis of phenanthrene-4-carboxylic acid.

In an attempt to improve the yield of cyano ketone (LXI), the ring closure was carried out in anhydrous hydrogen fluoride. Partial hydrolysis of the nitrile occurred and 1-keto-4-carbamoyl-1:2:3:4-tetrahydrophenanthrene (LXIX) was obtained. No acidic material was isolated. The action of anhydrous hydrogen fluoride on phenylacetonitrile, 1-cyano and 2-cyanonaphthalene was investigated under similar conditions, but the corresponding amides were not formed. A search of the literature revealed no allusion to the hydrolysis of nitriles with anhydrous hydrogen fluoride but instances are known where sulphuric acid has effected such a hydrolysis, e.g. Balabon and Manchester (15) obtained nicotinamide by allowing a solution of 3-cyanopyridine in 98% sulphuric acid to stand overnight at temperatures below 35°.

Acid hydrolysis of the keto amide proceeded almost quantitatively to the keto acid (LXII). A mixed melting point determination with authentic material was inconclusive but admixture of the respective methyl esters showed no depression in

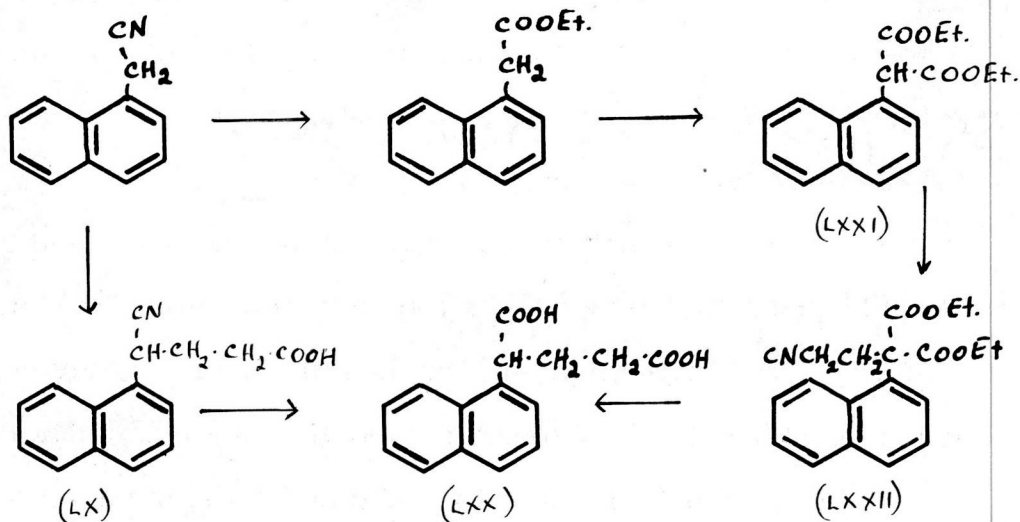
melting point. This, together with the analytical figures, sufficed to characterise the product.

Acid hydrolysis of δ -cyano- γ :1-naphthylbutyric acid resulted in an excellent yield of pure α :1-naphthylglutaric acid (LXX), which when cyclised with anhydrous hydrogen fluoride afforded a good yield of 1-keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene (LXII).



α :1-Naphthylglutaric acid has been synthesised by Ansell and Hey (16) by a somewhat lengthy route. Diethyl 1-naphthylmalonate (LXXI) was prepared in five stages from naphthalene and condensed with

acrylonitrile. The resulting diethyl 1-naphthyl-2'-cyanoethylmalonate (LXXII) on hydrolysis and decarboxylation yielded the α -substituted glutaric acid (LXX). This synthesis was a particular application of a general method for the preparation of α -substituted glutaric acids, but the reaction between arylacetonitriles and acrylic ester and subsequent hydrolysis of the condensation products seems of potential value in the general synthesis of α -arylglutaric acids.



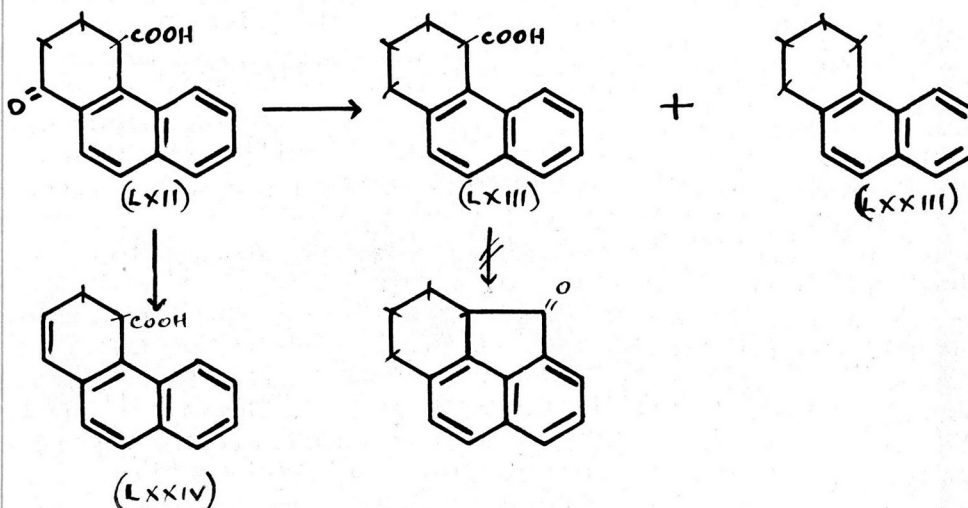
Ansell and Hey (14) found that the reduction of 1-keto-1:2:3:4-tetrahydrophenanthrene-4-carboxylic acid by the Wolff-Kishner method was accompanied by appreciable decarboxylation leading to 1:2:3:4-tetrahydrophenanthrene (LXXIII). In attempting to avoid this wasteful loss of material, other methods of reduction were investigated. An attempted reduction by the Clemmensen method under the conditions used by Bachmann and Struve (17) for the

reduction of 1-keto-1:2:3:4-tetrahydrophenanthrene gave an acidic mixture which could not be crystallised. Reduction with nickel-aluminium alloy in aqueous sodium hydroxide as employed by Papa, Schwenk and Whitman (18) yielded an acidic mixture which again could not be crystallised. Catalytic hydrogenation with platonic oxide (cf. Plattner, Furst and Keller (19)) proved unsuccessful and unchanged keto acid was returned. Thus, despite the accompanying decarboxylation, it was found necessary to employ the Wolff-Kishner method, and by following the procedure of Ansell and Hey (14), 1:2:3:4-tetrahydrophenanthrene-4-carboxylic acid (LXIII) was obtained in 60% yield along with 25% of the decarboxylated product (LXXIII).

Attempts were made to cyclise the reduced acid (LXIII) by a wide variety of methods. These included stannic chloride in benzene, anhydrous aluminium chloride in nitrobenzene and in carbon disulphide (all on the acid chloride), anhydrous hydrogen fluoride, polyphosphoric acid (cf. Koo (20)) and fusion with aluminium chloride-sodium chloride mixture, a method developed by Bruce, Sorrie and Thomson (21). In all cases, a non-ketonic neutral solid resulted which had no definite melting point but which melted over a wide range of temperature. Attempts to isolate a pure substance from the crude product by crystallisation, chromatography and continuous extraction with various solvents met

with failure.

From the nature of the product it was suspected that polymerisation of some kind had occurred and before carrying out further cyclisation experiments, it was decided to dehydrogenate 1:2:3:4-tetrahydrophenanthrene-4-carboxylic acid (LXIII) to the fully aromatic acid. Ansell and Hey (14) met with some difficulty in this respect due to the ease with which the tetrahydro acid decarboxylates. With palladium-charcoal, these authors obtained largely phenanthrene with only a trace of acidic material, while sulphur dehydrogenation of the methyl ester gave only a 10% yield of the desired product. Since these experiments involved heating the material to 200°C and above, it was hoped that the milder chloranil method would be more successful. However, treatment with chloranil in xylene overnight gave phenanthrene and 40% unchanged acid. Treatment with chloranil in nitrobenzene for a shorter time gave 40% phenanthrene and no acid at all. An attempted dehydrogenation by the method of Barnes (22) was unsuccessful. It appears therefore that 1:2:3:4-tetrahydrophenanthrene-4-carboxylic acid, under the conditions necessary for dehydrogenation, spontaneously decarboxylates.



In an attempt to obviate this difficulty, the methyl ester of the keto acid (LXII) was reduced by the Meerwein-Pondorff method. The oily hydroxy ester was dehydrated with formic acid and the mixture separated by chromatography into two main components. Hydrolysis of one fraction gave a small yield of 3:4-dihydrophenanthrene-4-carboxylic acid (LXXIV) but no pure substance could be obtained from the other.

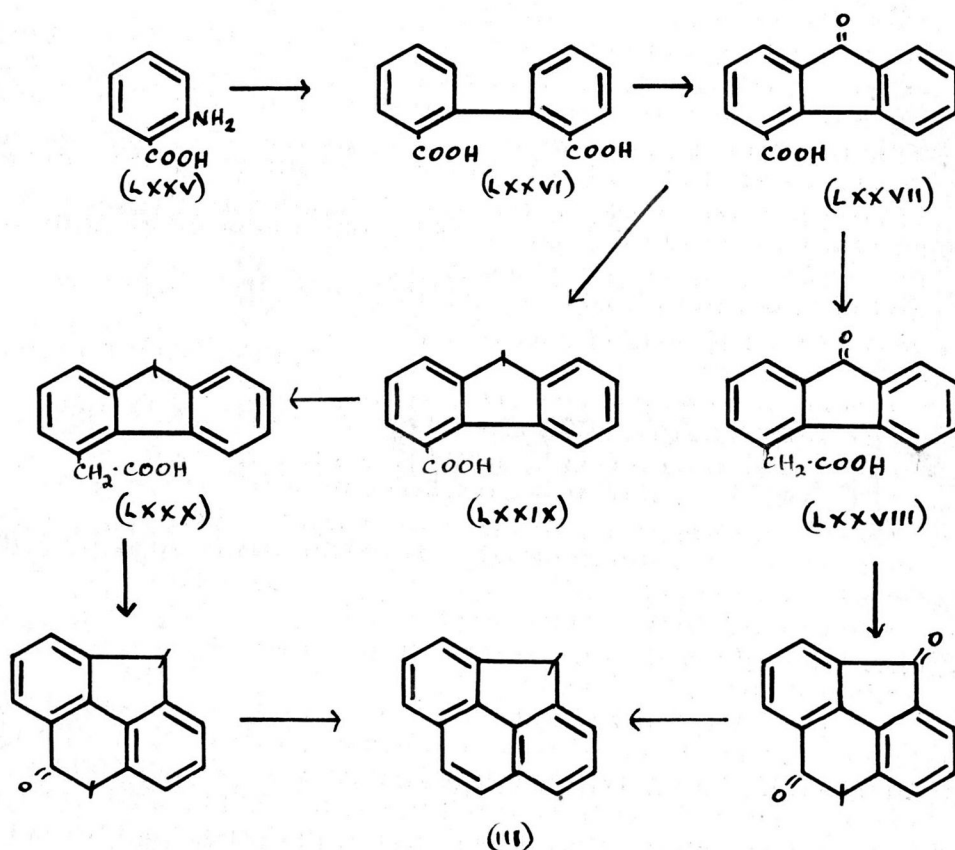
This method of synthesis was therefore abandoned due to the impure products isolated from the cyclisation of 1:2:3:4-tetrahydrophenanthrene-4-carboxylic acid and the inability to convert this acid to the aromatic phenanthrene-4-carboxylic acid.

SECTION A.

(ii) Synthesis of 4:5-Methylenephenanthrene from Fluorene.

The possibility of cyclising fluorene-4-acetic acid (LXXX) to 4:5-methylenephenanthrene (III) has already been remarked upon by Bachmann and Sheehan (23)

and indeed, these authors tried to effect the ring closure of both the fluorene- and fluorenone-4-acetic acids. Since their attempts were made only under those conditions sufficient to cyclise diphenyl-2-acetic acid (cf. Schonberg and Warren (24)), it was decided that a thorough investigation of this possible route to 4:5-methylenepheneanthrene was warranted. The proposed synthesis is set out below.



Diphenic acid (LXXVI) was prepared from anthranilic acid (LXXV) by the method of Atkinson and Lawler (25) and cyclised to fluorenone-4-carboxylic acid (LXXVII) with concentrated sulphuric acid as described by Bischoff and Adams (26). Fluorene-

and fluorenone-4-acetic acids were prepared following the conditions laid down by Bachmann and Sheehan (23). The Arndt-Eistert reaction on fluorenone-4-carboxylic acid (LXVII) gave fluorenone-4-acetic acid (LXXVIII) in 40% yield. The initial reaction product, the methyl ester, was very impure and required to be crystallised several times, thus accounting for the low yield of acid. Reduction of fluorenone-4-carboxylic acid (LXXVII) with zinc and caustic soda gave the corresponding fluorenol which was further reduced with phosphorus and iodine to fluorene-4-carboxylic acid (LXXIX). The Arndt-Eistert reaction yielded fluorene-4-acetic acid (LXXX).

Attempts to cyclise fluorenone-4-acetic acid (LXXVIII) were made under a variety of conditions. Anhydrous aluminium chloride in nitrobenzene (on the acid chloride) sulphuric acid at room temperature and at 100°, anhydrous hydrogen fluoride and polyphosphoric acid (cf. Koo (20)) gave mere traces of non-acidic material together with much unchanged acid. Fusion with aluminium chloride-sodium chloride mixture (cf. Bruce, Sorrie and Thomson (21)) resulted in extensive charring, and only a trace of acidic material was recovered.

Attempts to ring close fluorene-4-acetic acid (LXXX) with anhydrous hydrogen fluoride and polyphosphoric acid gave appreciable amounts of unchanged acid along with smaller quantities of neutral products. Attempts to purify these by crystallisation and

chromatography were unsuccessful. An attempted cyclisation of the acid chloride with anhydrous aluminium chloride in nitrobenzene gave some neutral product and only a trace of acid. Again, the non-acidic fraction could not be purified. Attempted ring closures in concentrated sulphuric acid resulted in the formation of water soluble products, sulphonation presumably having occurred.

Thus, although some neutral product was isolated in certain of the cyclisation experiments, this method of approach was clearly of no value in the synthesis of 4:5-methylenepnenanthrene and was abandoned.

SECTION A.

(iii) Syntheses of 4:5-Methylenepnenanthrene from Acenaphthene.

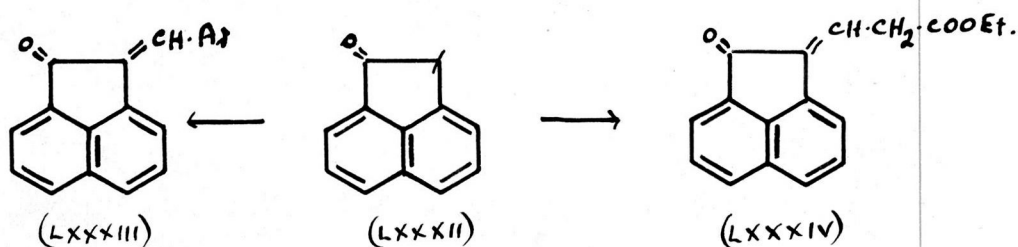
a) Experiments with 1-Acenaphthenone.

1. In their original synthesis of 4:5-methylene-phenanthrene, Bachmann and Sheehan (4) oxidised acenaphthene to acenaphthenol and converted the alcohol to 1-bromoacenaphthene. The bromine atom was replaced with a malonic acid group, thus introducing the side chain which was lengthened by the Arndt-Eistert method (cf. introduction p. 3).

1-acenaphthenol may be further oxidised to 1-acenaphthenone (LXXXII) which has a reactive methylene group in the 2-position. It was hoped that the additional step involved in the preparation of starting material would be offset if the required side chain could be introduced in its entirety, thus

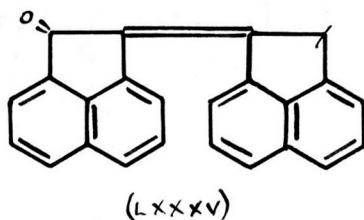
avoiding any subsequent chain lengthening process.

The reactivity of the methylene group in 1-acenaphthenone has been demonstrated by the formation of arylidene derivatives (LXXXIII) with aromatic aldehydes (cf. (27), (28) and (29)), and it was hoped that a similar condensation could be effected with ethyl sodium formylacetate to give the alkylidene derivative (LXXXIV).



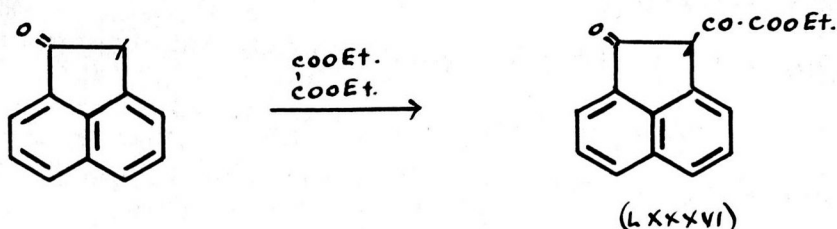
1-acenaphthenone (LXXXII) was prepared as described by Fieser and Cason (30). Ethyl sodium formylacetate was prepared from ethyl acetate and ethyl formate by the method of Cogan (31) as modified by McElvain and Clarke (32).

Attempts were made to condense 1-acenaphthenone with ethyl sodium formylacetate in alcoholic solution but self-condensation of the ketone occurred and the dimeric biacenaphthylidenone (LXXXV) was the only product isolated. An experiment in methylene chloride under acid conditions gave the same result.



A series of condensations was also carried out between 1-acenaphthenone and cyanoacetal, prepared by the method of Hartung and Adkins (33). Reactions in boiling acetic acid with piperidine acetate as catalyst yielded dark sticky oils while an experiment at room temperature gave unchanged acenaphthenone. Attempts to effect the condensation in warm alcoholic solution containing sodium hydroxide or in methylene chloride solution saturated with dry hydrogen chloride resulted in the formation of biacenaphthylidenone (LXXXV).

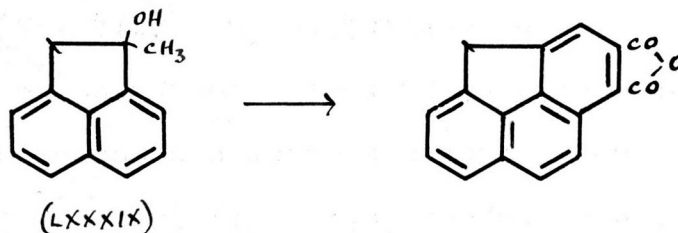
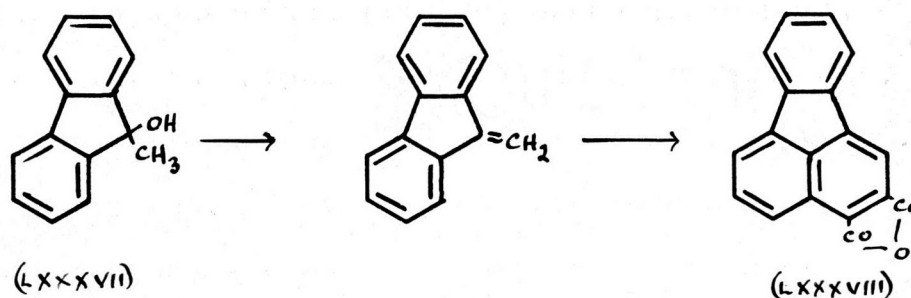
Graebe and Jequier (34) describe the formation of this substance by warming an alcoholic solution of acenaphthenone with alkali, and Henderson (35), in attempting the Stobbe reaction on acenaphthenone, found that self-condensation preferentially occurred. Duthie and Plant, however, (36) have successfully condensed acenaphthenone with oxalic ester under alkaline conditions to give ethyl 1-acenaphthenone-2-glyoxalate (LXXXVI).



Presumably, of the two competing reactions, the condensation of the ester with acenaphthenone was the faster, and since their experiments were

conducted below 5°C, the temperature would also seem to be an important factor.

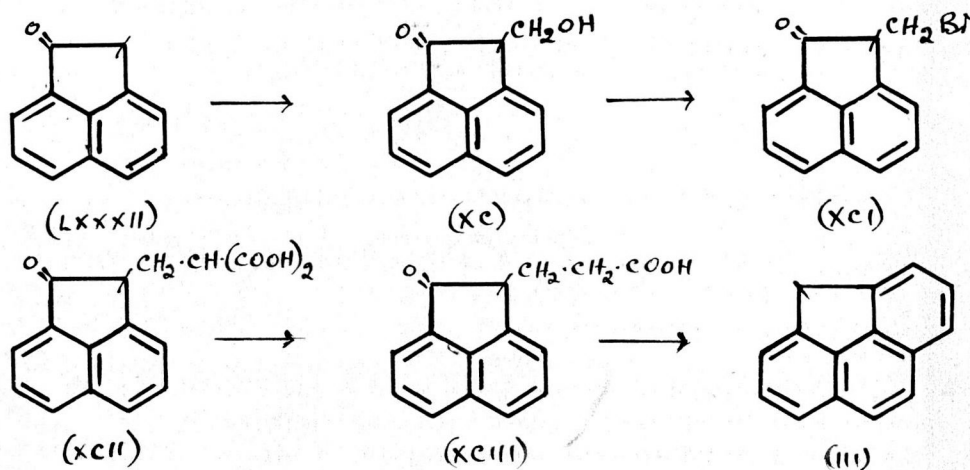
2. 1-Acenaphthenone reacts normally with Grignard reagents and it was hoped to carry out a synthesis of 4:5-methylenephenanthrene by a method analogous to that developed by Campbell and Wang (37) for the synthesis of fluoranthene from fluorenone. Fluorenone and methylmagnesium iodide gave the carbinol (LXXXVII) which when heated with maleic anhydride in acetic anhydride, simultaneously dehydrated and underwent the diene reaction affording the fully aromatic fluoranthene-3:4-dicarboxylic anhydride (LXXXVIII).



Treatment of 1-acenaphthenone with methylmagnesium iodide as described by Brown and Hammick (38) gave 1-hydroxy-1-methylacenaphthenone (LXXXIX). This, with maleic anhydride in acetic anhydride, yielded a

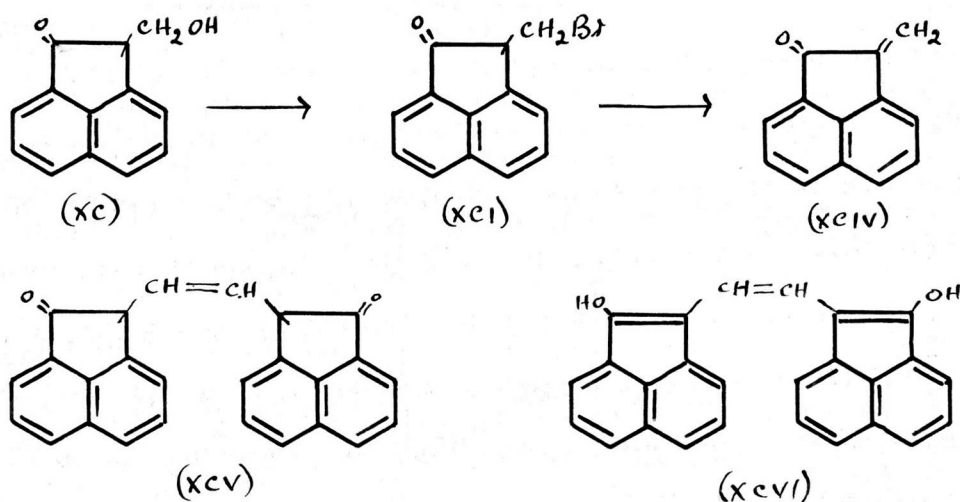
brown solid which could not be purified. Heating with calcium oxide gave a red oil which, when chromatographed on alumina, afforded a series of oils, none of which formed a picrate. In one experiment, the crude carbinol (LXXXIX) in ether was treated with maleic anhydride at room temperature. Evaporation of the mixture on the steam bath gave an oily solid which afforded a small amount of biacenaphthylidenone (LXXXV). It can only be presumed that the Grignard reaction had not gone to completion and heating the unchanged acenaphthenone with maleic anhydride gave the self-condensation product. Duthie and Plant (36) in attempting to condense acenaphthenone with anthranilic acid obtained a similar result.

3. Attention was turned to a paper by Gault and Kalopissis (39) describing the preparation of 1-hydroxymethylacenaphthenone (XC) by the condensation of acenaphthenone and formaldehyde. It was intended to carry out the malonic ester synthesis on the corresponding bromide (XCI) and decarboxylate the substituted malonic acid (XCII). The 1-acenaphthenone-2-propionic acid (XCIII) so obtained, on ring closure, reduction and dehydrogenation, would then lead to 4:5-methylenephenanthrene (III).



In the preparation of 1-hydroxymethyl-2-acenaphthenone (XC), the instructions of Gault and Kalopissis were carefully followed, but their results could not be duplicated and a most impure product was obtained in a yield lower than that claimed by these workers. A quantity of almost pure material was isolated from the crude product but the small yield prohibited the use of this reaction in the synthesis. Nevertheless, an attempt was made to form 1-bromomethyl-2-acenaphthenone (XCI) with phosphorus tribromide. Since the starting material was quite insoluble in ether and only sparingly soluble in cold chloroform, the phosphorus tribromide was added to a hot chloroform solution of the ketol. An orange colouration immediately spread throughout the solution and a bright orange solid, crystallising from glacial acetic acid, was isolated from the reaction mixture. The product decolourised permanganate solution, failed to form a dinitrophenylhydrazone derivative and analysed for $C_{15}H_8O$. A molecular weight determination

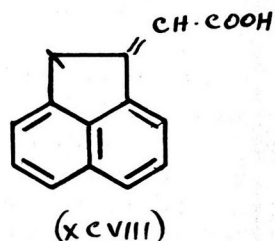
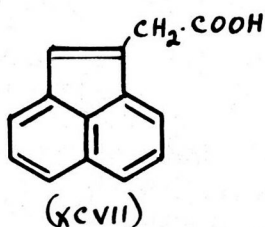
indicated the presence of a "dimer". It is suggested that the first formed bromomethylacenaphthenone (XCI) spontaneously lost hydrogen bromide affording the methylene compound (XCIV), two molecules of which linked up to give the "dimer" (XCV), probably existing in the enolic form (XCVI) thus increasing the conjugation in the molecule and accounting for its colour.



4. Since the first attempted synthesis of 4:5-methylenepheneanthrene involved the Reformatsky reaction on tetrahydroacenaphthenone (cf. introduction p. 2), it was of interest to carry out this reaction on acenaphthenone itself.

Acenaphthenone reacted with ethyl bromoacetate and zinc to give a mixture of unsaturated acids, the hydroxy esters first formed undergoing spontaneous dehydration. The acids were separated quite fortuitously and subsequent attempts to repeat the

separation were unsuccessful. Attempted chromatographic separation of the methyl esters was also unsuccessful. Of the two acids, one was almost colourless (m.p. 239°) and the other bright yellow in colour (m.p. 133°). The latter, in view of its colour, was presumed to be 1-acenaphthyleneacetic acid (XCVII) and the former 1-acenaphthylideneacetic acid (XCVIII).



In the initial experiments, zinc dust was used and up to 40% of biacenaphthylidenone was isolated from the reaction. This type of self-condensation of ketones is not unknown in the Reformatsky reaction and according to Shriner (40) is catalysed by zinc salts. By using large excesses of ethyl bromoacetate and zinc (in the form of wool), the dimeric material was formed in smaller amounts and the yields of unsaturated acids increased accordingly. Yields of 76% were ultimately obtained. Hydrogenation of the crude mixture of acids in ethyl acetate with platonic oxide as catalyst gave 1-acenaphthenylacetic acid.

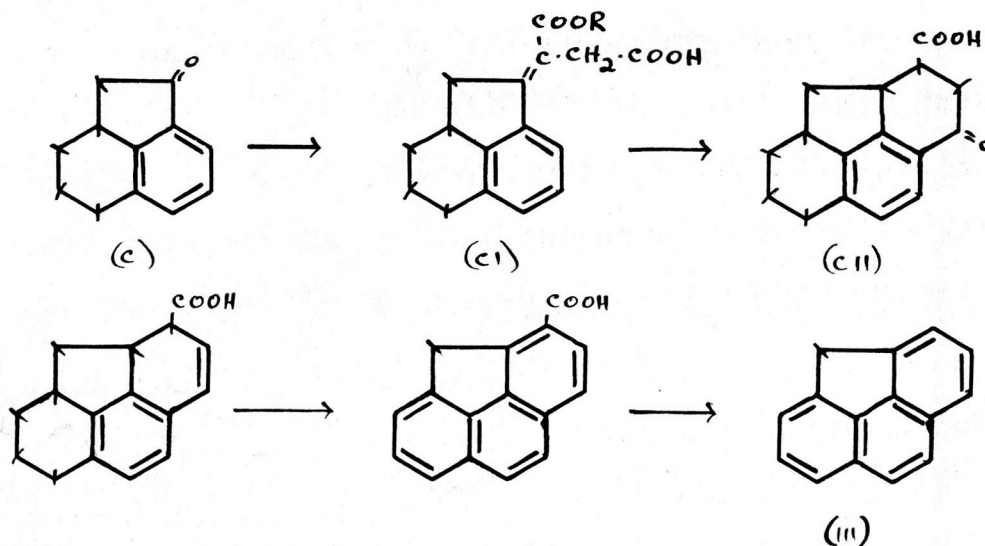
In view of the two-stage oxidation process involved in the preparation of 1-acenaphthenone, and the moderate yields obtained in the subsequent

reactions, it is doubtful if this method of synthesising 1-acenaphthenylacetic acid presents any advantage over the method developed by Bachmann and Sheehan (4).

SECTION A.

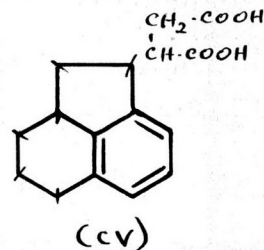
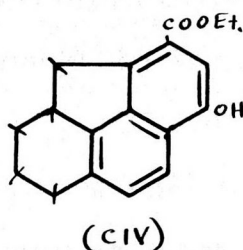
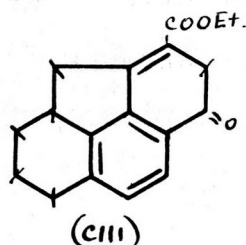
(iii) (b). The Stobbe Reaction on Tetrahydroacenaphthenone.

The extreme ease with which acenaphthenone undergoes self-condensation detracts from its usefulness in synthetic work. An attempted Stobbe reaction on acenaphthenone carried out by Henderson (35) gave biacenaphthylidenone as the sole product. It was decided to investigate the same reaction on tetrahydroacenaphthenone.



2a:3:4:5-Tetrahydroacenaphthenone (C) was prepared in good overall yield by the excellent method of Johnston and Glen (41) and condensed with diethyl succinate in t-butyl alcohol to give a rather impure half-ester (CI, R = Et). An attempted ring

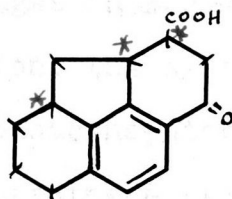
closure of the crude product by the anhydrous zinc chloride-acetic anhydride method of Fieser and Hershberg (42) was unsuccessful but cyclisation in anhydrous hydrogen fluoride gave a small amount of ethyl 1-keto-1:2:5:6:7:8-hexahydro-4:5-methylene-phenanthrene-3-carboxylate (CIII) which probably exists in the enolic form (CIV). No dinitrophenylhydrazones derivative could be prepared.



Attempted reduction of the unsaturated acids (CI, R = H) with 4% sodium amalgam gave an oil. Catalytic hydrogenation with 5% palladium on charcoal yielded a solid product which could not be crystallised but which was assumed to be the tetrahydroacenaphthenyl-1-succinic acid (CV). Cyclisation of this crude material with anhydrous hydrogen fluoride afforded an acidic oil from which there was isolated a 30% yield of 1-keto-3-carboxy-1:2:3:4:5:6:7:8-octahydro-4:5-methylenepheneanthrene (CII). Cyclisation with polyphosphoric acid (cf. Koo (20)) gave an even smaller yield of keto acid.

Although the precursors had not been purified, the mixture of products obtained on cyclisation could have been due to the presence of stereoisomers. The keto acid (CII) contains three asymmetric centres

(carbon atoms 3, 4 and 5) and in each case the hydrogen atoms may lie above or below the plane of the rings, giving four possible geometric isomers.



(cII)

With this possibility in mind, it was decided to attempt a synthesis of 4:5-methylenephenanthrene by this route without isolating the intermediate compounds. The crude keto acid (CII) was treated with sodium borohydride (cf. Chaikin and Brown (43)) and the product dehydrated with 90% formic acid to form the hexahydro compound. The crude solid was then treated with chloranil in xylene and a very impure acid was isolated in poor yield which could not be purified.

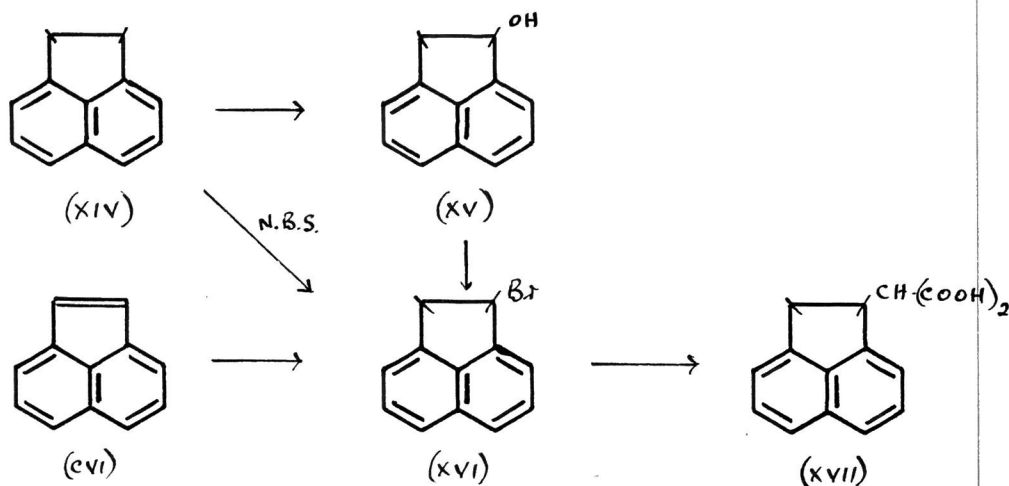
In general, the method of synthesis did not prove satisfactory and work was discontinued.

SECTION A.

(iii) (c) The Hydrobromination of Acenaphthylene.

Reference has already been made to the synthesis of 4:5-methylenephenanthrene by Bachmann and Sheehan (4) in which acenaphthenol (XV) was treated with phosphorus tribromide and the resulting 1-bromo-acenaphthene (XVI) reacted with malonic ester to give 1-acenaphthenylmalonic acid (XVII). The lead

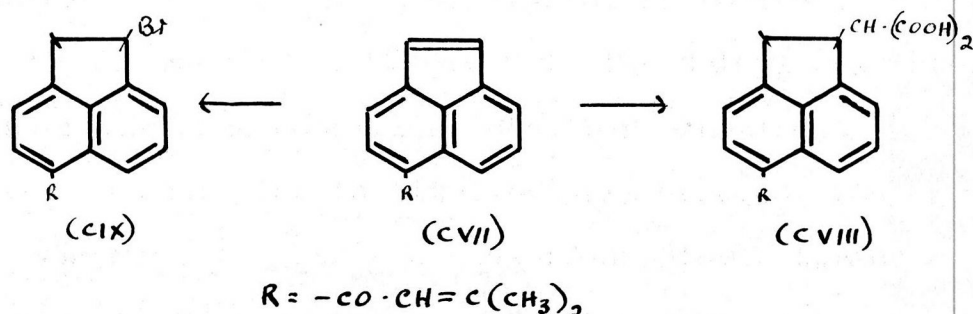
tetraacetate oxidation of acenaphthene to acenaphthenol, while furnishing good yields of product, is one of the longer stages in Bachmann's method and by avoiding this oxidation, the synthesis is shortened considerably. 1-Bromoacenaphthene may be prepared in one step from acenaphthene by the N-bromosuccinimide method of Julia (44). This method was examined and the product condensed with malonic ester to give the substituted malonic acid (XVII) in 50% yield. A much easier method of preparing 1-bromoacenaphthene was found in the hydrobromination of acenaphthylene (CVI).



Acenaphthylene (CVI) was simply dissolved in ether and the mixture saturated with bromine free hydrogen bromide gas. The crude product required no purification and subsequent condensation with malonic ester gave 1-acenaphthenylmalonic acid (XVII) in 88% yield (based on acenaphthylene). It is evident that this simple step improves upon Bachmann's method,

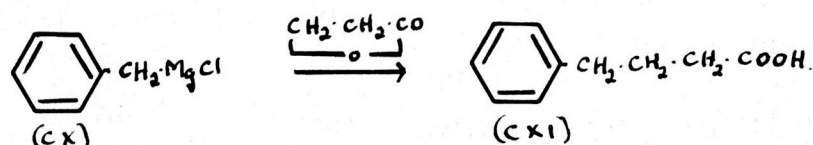
involving a considerable saving of time and materials. Further comment on the use of the hydrobromination of acenaphthylene is made in the appendix to the Discussion.

Two recent papers by Fuson et al. (45) and (46) describe the Michael condensation of 5-mesitylacenaphthylene (CVII) with diethyl malonate giving 5-mesityl-1-acenaphthenylmalonic acid (CVIII) in good yield. Treatment of 5-mesitylacenaphthylene (CVII) with 48% hydrobromic acid gave 80% of 1-bromo-5-mesitylacenaphthene (CIX).

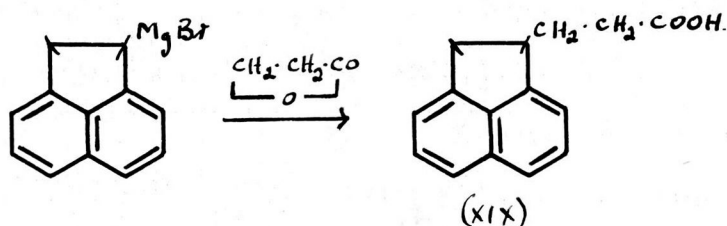


These reactions were also attempted on 5-nitro-acenaphthylene but without success, due no doubt to the deactivating influence of the nitro group. It may be mentioned that experiments previously carried out in this department showed that the reactivity of acenaphthylene itself in the Michael condensation was too low for the reaction to be of value.

Gresham (47) in studying the chemistry of β -propiolactone found that reaction with benzylmagnesium chloride (CX) gave γ -phenylbutyric acid (CXI).



It was hoped that a similar reaction with 1-bromoacenaphthene would give 1-acenaphthenylpropionic acid (XIX),



1-Bromoacenaphthene reacted briskly with magnesium until the metal surface became clogged up with oily deposits when the reaction slowed down and eventually stopped. Despite this, β -propiolactone was added to the mixture and a complex seemed to form. On decomposition however, no acidic products were isolated and attempts to purify the non-acidic fraction by chromatography gave a series of oils, none of which could be crystallised.

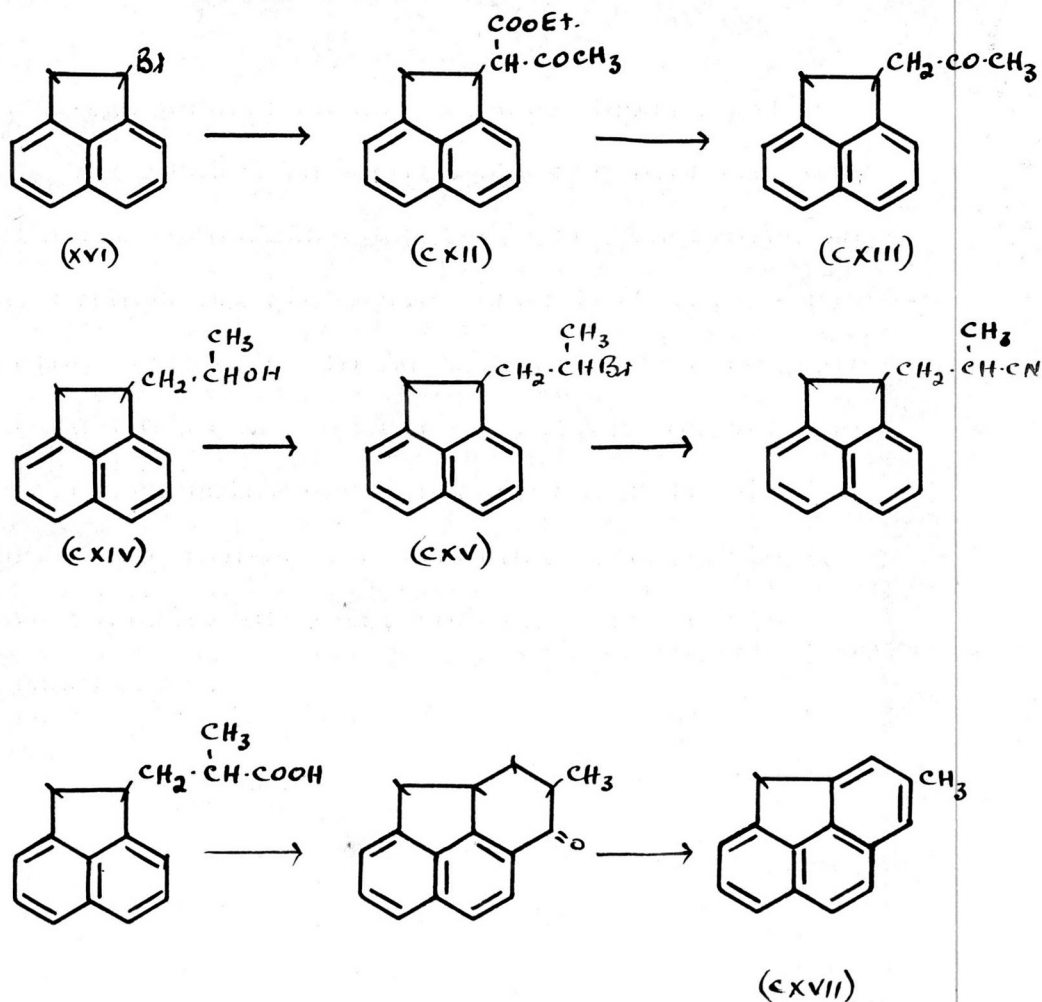
SECTION B.ATTEMPTED SYNTHESSES OF
METHYL-4:5-METHYLENEPHENANTHRENES.

Only three alkyl derivatives of 4:5-methylene-phenanthrene are known, namely the 1-ethyl, 1-methyl and 3-ethyl compounds (cf. introduction p. 5).

Having found a rapid and easy way of preparing 1-bromoacenaphthene, it was decided to exploit this in attempting the synthesis of the 2- and 3-methyl derivatives.

SECTION B.

(1) Synthesis of 2-Methyl-4:5-methylenepheneanthrene (CXVII)



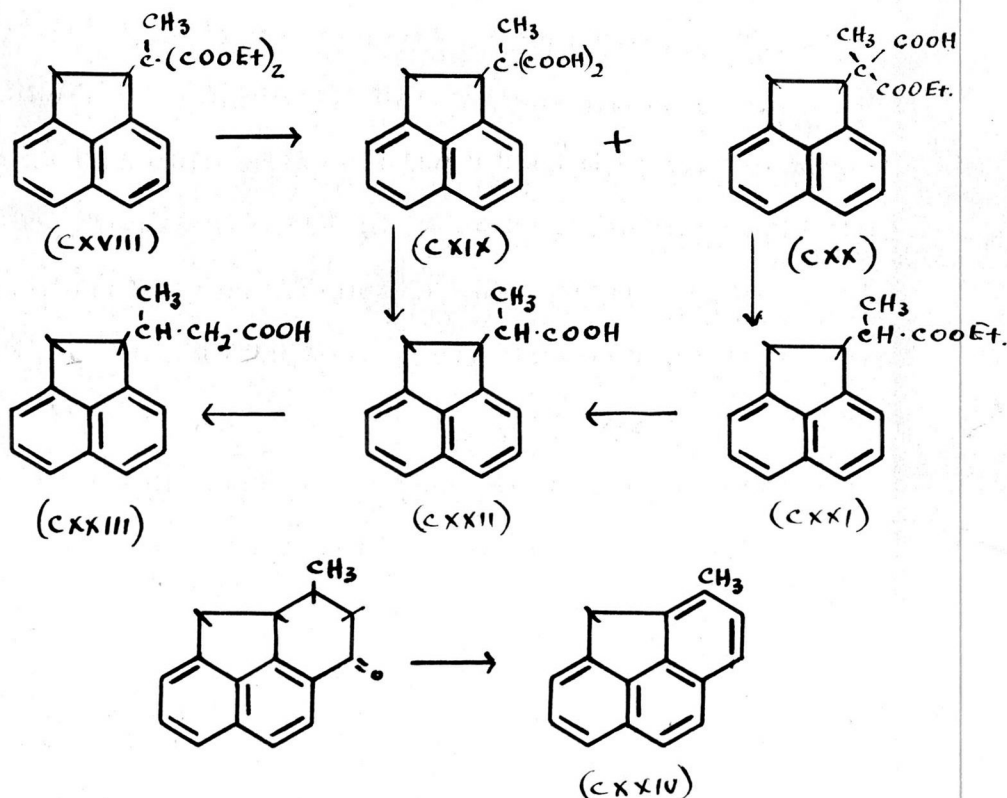
1-Bromoacenaphthene was condensed with ethyl acetoacetate by the method of Campbell, Corrigan and Campbell (29). Ketonic cleavage of the ester (CXII) gave 70% of 1-acenaphthenylacetone (CXIII) and 21% of 1-acenaphthenylacetic acid. Reduction of the ketone with lithium aluminium hydride afforded the alcohol (CXIV), treatment of which with phosphorus tribromide gave an oil containing bromine. The crude bromide (CXV) on boiling with potassium cyanide in aqueous alcohol yielded a product which showed a weak test for nitrogen, but acid hydrolysis gave no acidic material. The synthesis was abandoned at this stage.

SECTION B.

(ii)

Syntheses of 3-Methyl-4:5-methylenephenanthrene (CXXIV)

(a)

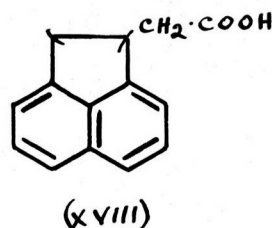
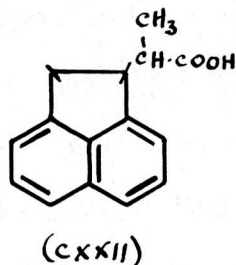


Diethyl methylmalonate, prepared by the method of Cox (48), was condensed with 1-bromoacenaphthene giving the disubstituted malonate (CXVIII). Hydrolysis of the diester under the conditions used by Blicke and Feldkamp (49) in their general synthesis of substituted malonic acids, gave an acidic mixture of 1-acenaphthenylmethylmalonic acid (CXIX) and the half-ester (CXX) (cf. Campbell, Corrigan and Campbell (29)). The analysis figures for the malonic acid showed high values for carbon and hydrogen, possibly due to the presence of some decarboxylated product (CXXII). The mixture of hydrolysis products gave on decarboxylation α :1-acenaphthenylpropionic acid (CXXII) together with the ethyl ester (CXXI) hydrolysis of which gave a further amount of acid. The crude yield of acenaphthenylpropionic acid (CXXII) was 73% but purification by crystallisation proved unaccountably wasteful and the yield of pure product was only of the order of 30% (based on acenaphthylene). Increasing the time allowed for decarboxylation made little difference to the final yield. The same results were obtained when the 1-bromoacenaphthene was prepared by the phosphorus tribromide treatment of acenaphthenol (cf. Bachmann and Sheehan (4)).

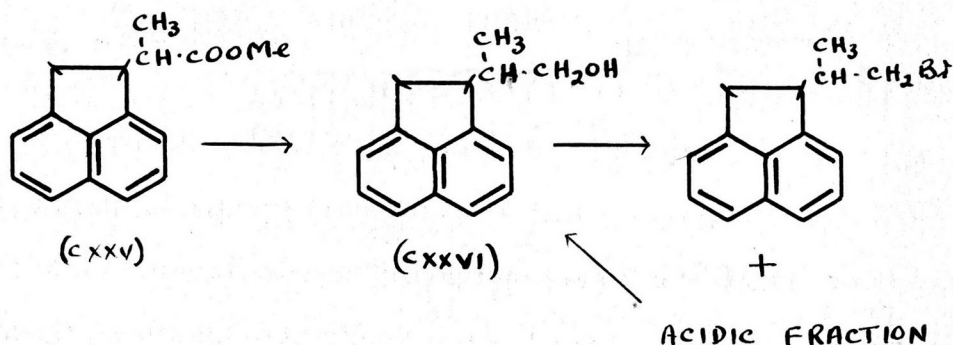
Attempts to prepare β :1-acenaphthenylbutyric acid (CXXIII) by the Arndt-Eistert reaction unexpectedly failed. The acid chloride of α :1-acenaphthenylpropionic acid (CXXII) was prepared with thionyl

chloride and when added to an ethereal solution of diazomethane, gave a dark orange coloured precipitate, presumably of diazoketone, although very little nitrogen was evolved. This was filtered off and attempted rearrangements with silver oxide in methanol were made on this solid and on the oily residue obtained by the low temperature evaporation of the ethereal filtrate. In each case, the material was only sparingly soluble in hot methanol and no evolution of nitrogen was observed. Hydrolysis gave little or no acidic material. α :1-Acenaphthenylpropionyl chloride, when prepared under milder conditions gave no precipitate of diazoketone on addition to diazomethane, although a little gas was evolved. The ultimate product was an oily acid which could not be purified.

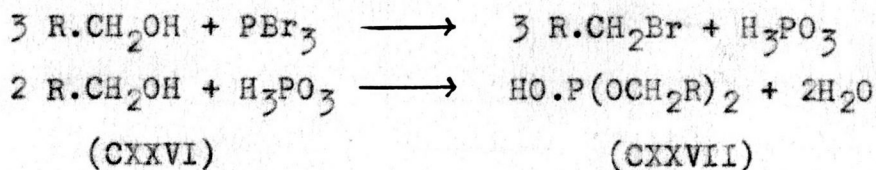
Several attempts were made to carry out this important stage in the synthesis. Failure to do so is difficult to understand in view of the fact that 1-acenaphthenylacetic acid (XVIII) undergoes the reaction readily (cf. Bachmann and Sheehan (4)).



It was then decided to lengthen the side chain of $\alpha:1$ -acenaphthenylpropionic acid (CXXII) via the corresponding alcohol and bromide. Reduction of the methyl ester (CXXV) with lithium aluminium hydride proceeded smoothly to the alcohol (CXXVI). Treatment with phosphorus tribromide at room temperature gave a neutral fraction containing labile bromine and an acidic fraction, which on treatment with boiling methanol containing a little concentrated sulphuric acid, afforded the parent alcohol again.

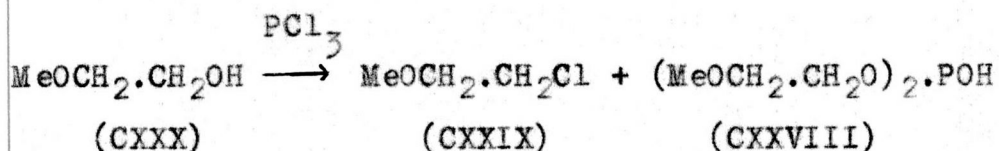


The occurrence of this acid was probably due to the formation of a phosphite ester (CXXVII) by the interaction of the alcohol (CXXVI) with the phosphorous acid produced in the bromination reaction.

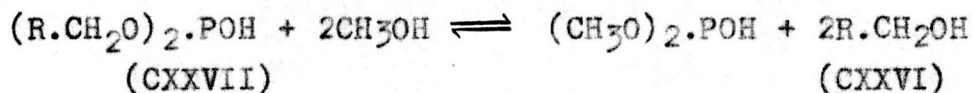


The treatment of alcohols with phosphorus trichloride has been used as a method of preparing phosphite esters. In this way, for example, Abramov and Militskova (50) obtained the phosphite

ester (CXXVIII) together with 2-methoxyethylchloride (CXXIX) from 2-methoxyethanol (CXXX).



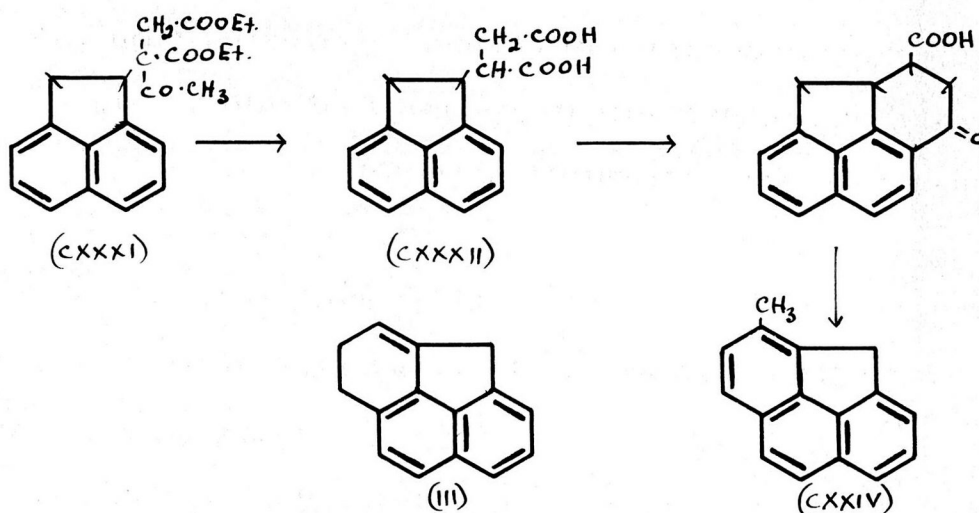
Since the regeneration of the alcohol (CXXVI) was effected under anhydrous conditions, it seems likely that the mechanism was one of ester exchange rather than one of hydrolysis, the large excess of methanol present displacing the equilibrium to the right.



An attempt to react β :1-acenaphthenylethylbromide with magnesium was unsuccessful, treatment of the reaction mixture with solid carbon dioxide giving a non-acidic oil containing bromine, but no acidic material. Treatment of the bromo-compound with butyllithium and then solid carbon dioxide gave the same result. An attempt to convert the bromide into the corresponding nitrile was also unsuccessful, the product containing bromine but no nitrogen.

Since attempts to lengthen the side chain of α :1-acenaphthenylpropionic acid (CXXII) proved unsuccessful, the synthesis was abandoned.

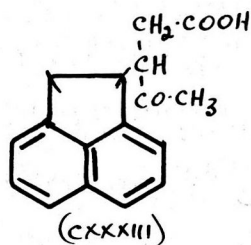
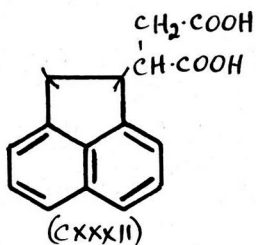
b) By reacting 1-bromoacenaphthene with α -aceto-succinic ester and hydrolysis of the condensation product (CXXXI) to 1-acenaphthenylsuccinic acid (CXXXII), it was hoped that a synthesis might be found which could be modified to give either 3-methyl-4:5-methylenephenanthrene (CXXIV) or the parent hydrocarbon itself (III).



Diethyl α -acetosuccinic ester, prepared by the method of Conrad (51), was condensed with 1-bromo-acenaphthene. The reaction appeared to proceed readily but hydrolysis of the product (CXXXI) with aqueous potassium hydroxide gave 1-acenaphthenylsuccinic acid (CXXXII) which was obtained in a pure state only after repeated crystallisation. In subsequent experiments, no pure material could be isolated at all.

Since this condensation is of the acetoacetic ester type, one might expect at least two products from the hydrolysis, according to whether ketonic or

acid cleavage occurred. These would be the succinic acid (CXXXII) and the acetopropionate (CXXXIII).

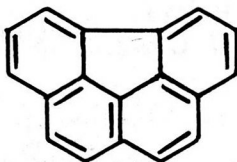


For this synthetic method to be of value, the hydrolysis conditions would require to be carefully adjusted. Unfortunately time did not permit more than a cursory examination before work was discontinued.

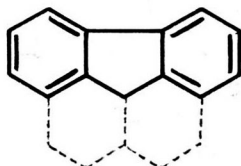
SECTION C.ATTEMPTED SYNTHESSES OF 2:13-BENZFLUORANTHENE.

The hydrocarbon 2:13-benzfluoranthene (XLVII) has been synthesised by Campbell and Reid (10) by two methods (cf. introduction p. 9). Since the starting material for both syntheses was the inaccessible 4:5-methylenephenanthrene, it was decided to explore the possibility of synthesising 2:13-benzfluoranthene by more direct methods.

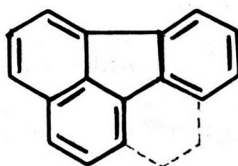
As in the case of 4:5-methylenephenanthrene, 2:13-benzfluoranthene (XLVII) may be regarded as being built up from various simpler ring systems, particularly fluorene (LVII), fluoranthene (CXXXVIII), 3:4-benzphenanthrene (CXXXIX) and 4:5-methylenephenanthrene.



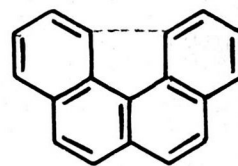
(XLVII)



(LVII)



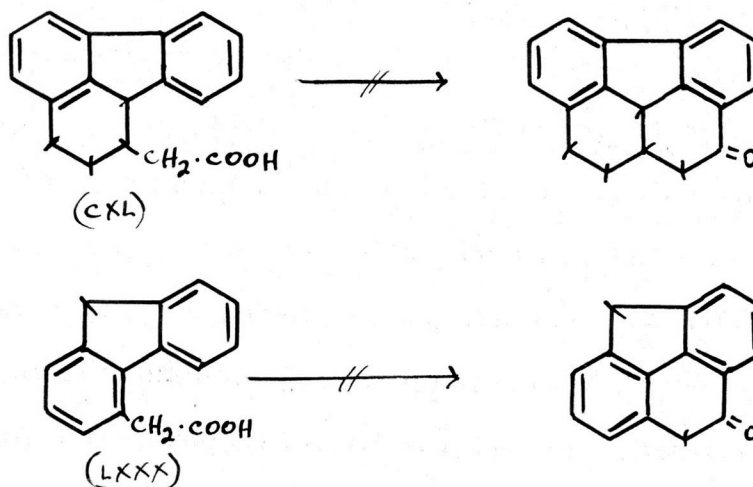
(CXXXVIII)



(CXXXIX)

A synthesis of 2:13-benzfluoranthene from fluoranthene was attempted by Swan (52) who was

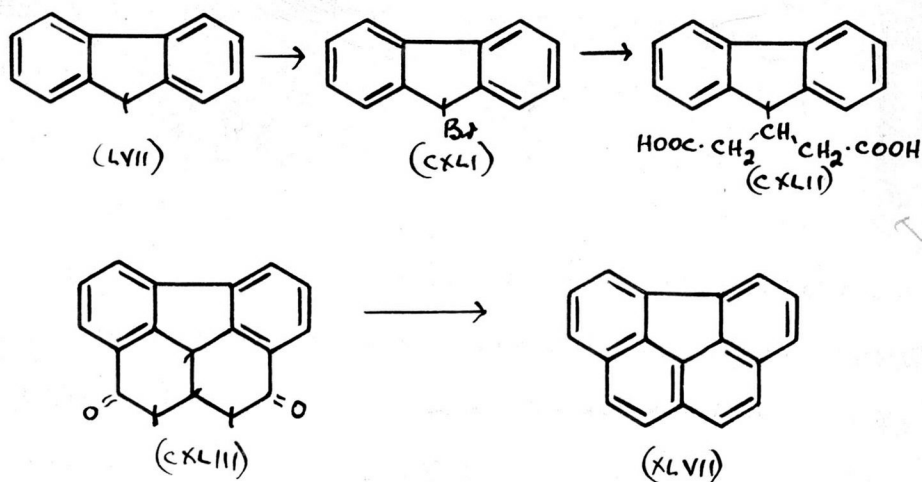
unable to cyclise 1:2:3:4-tetrahydrofluoranthene-2-acetic acid (CXL). A parallel may be drawn with the attempted ring closure of fluorene-4-acetic acid (LXXX) described in section A of this thesis.



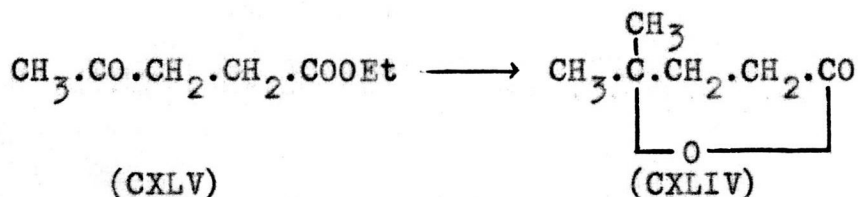
Since the original syntheses of 2:13-benzfluoranthene were made from 4:5-methylenepheneanthrene, it remained to explore syntheses from fluorene (LVII) and 3:4-benzphenanthrene (CXXXIX).

SECTION C.

(1) Synthesis of 2:13-Benzfluoranthene from Fluorene.

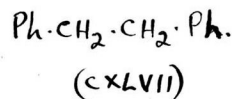
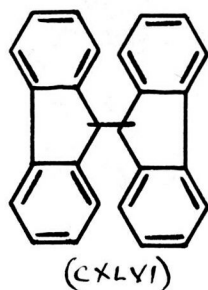


It was hoped that the Grignard reaction between 9-fluorenyl-magnesium bromide and diethyl acetone-dicarboxylate would lead to β :9-fluorenylglutaric acid (CXLII). Grignard reactions with keto esters have been effected on several occasions, e.g. Noyes and Manuel (53) obtained isocapro lactone (CXLIV) by treating laevulinic ester (CXLV) with methylmagnesium iodide. Other examples are to be found in the literature.



Cyclisation of the glutaric acid (CXLII) would give the diketone (CXLIII) leading to the desired hydrocarbon (XLVII).

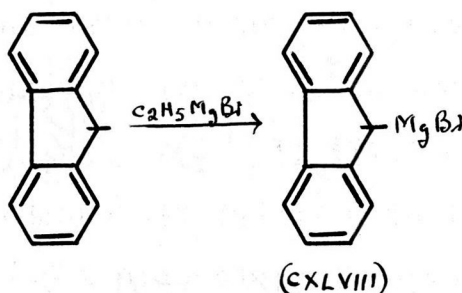
9-Bromofluorene (CXLI) was prepared by the N-bromosuccinimide method of Fuson and Porter (54). Treatment with magnesium unexpectedly gave difluorenyl (CXLVI) by a Fittig type of reaction, the bromine atoms being eliminated as magnesium bromide.



Miller and Bachmann (55) isolated this same hydrocarbon in attempting to react 9-fluorenyl-magnesium bromide with benzyl bromide. The expected

9-benzylfluorene was not formed, but a double coupling reaction gave difluorenyl (CXLVI) and diphenylethane (CXLVII). A similar reaction took place between 9-chlorofluorene and various Grignard reagents.

9-Fluorenylmagnesium bromide (CXLVIII) was prepared by the method of Miller and Bachmann (55) in which fluorene is treated with ethylmagnesium bromide. On addition of diethyl acetonedicarboxylate to the Grignard reagent, a complex seemed to form

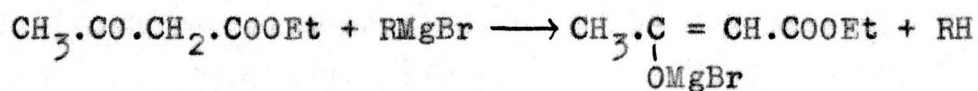


but hydrolysis of the reaction mixture gave fluorene and only a trace of acidic material. In a further attempt to obtain the glutaric acid (CXLII) fluorene was treated with n-butyllithium following the procedure of Miller and Bachmann (55), and diethyl acetonedicarboxylate added to the resulting 9-fluorenyllithium. As before, a complex seemed to form, but the sole reaction product proved to be fluorene. An experiment in which phenylmagnesium bromide was treated with the keto ester resulted in the formation of a complex, but no reaction product could be isolated.

No reference in the literature could be found to



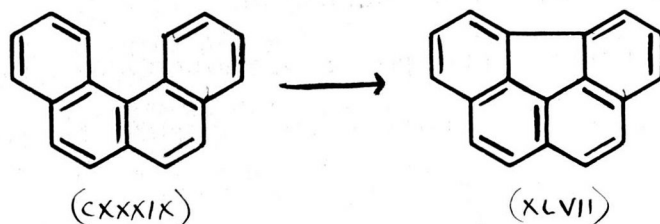
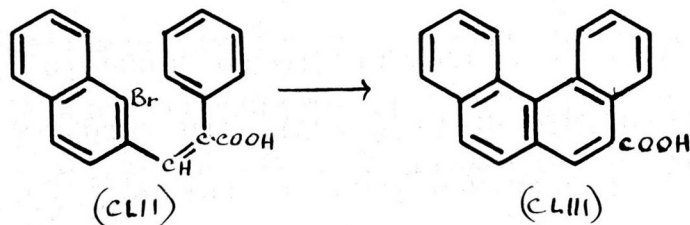
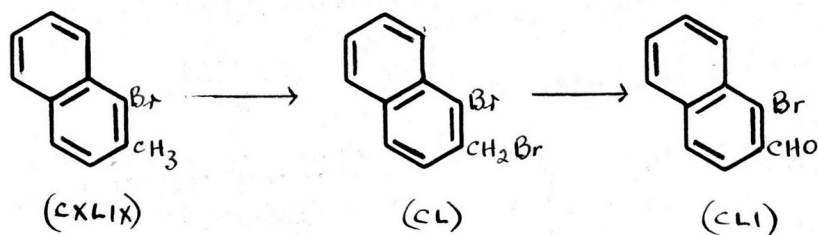
the reaction of Grignard reagents with diethyl acetonedicarboxylate. According to Ghigi (56), Grignard reagents react with compounds of the acetoacetic ester type to give the hydrocarbon and the magnesium derivative of the enolic form of the ketone.



From the above observations, it would appear that a similar reaction has occurred in the present instance.

SECTION C.

(ii) Synthesis of 2:13-Benzfluoranthene from 3:4-Benzphenanthrene.



The structures of 2:13-benzfluoranthene (XLVII) and 3:4-benzphenanthrene (CXXXIX) are closely related. They differ only in that the latter lacks the bridging bond between the 4' and 5 positions, and it was decided to attempt the introduction of this bond by a forced dehydrogenation reaction.

The synthesis of 3:4-benzphenanthrene (CXXXIX) was carried out by the method of Hewett (57) and requires little comment. Nuclear bromination of 2-methylnaphthalene Adams and Binder (58) gave 1-bromo-2-methylnaphthalene (CXLIX) which was then brominated in the side chain with N-bromosuccinimide, as described by Bergmann and Szmuszkowicz (59). Oxidation of the dibromide (CL) with hexamine in boiling glacial acetic acid (Hewett (60)) afforded 1-bromo-2-naphthaldehyde (CLI), which reacted with sodium phenylacetate in acetic anhydride to give α -phenyl- β :2-(1-bromonaphthyl)-acrylic acid (CLII). Fusion with potassium hydroxide afforded 2-carboxy-3:4-benzphenanthrene (CLIII), decarboxylation of which gave the hydrocarbon (CXXXIX).

Various attempts to effect the internal cyclisation of 3:4-benzphenanthrene by fusion at various temperatures with anhydrous aluminium chloride or mixtures of this reagent with sodium chloride, afforded highly fluorescent yellow oils. When chromatographed on alumina, no development into bands was apparent and fractions of the eluate gave on

evaporation a series of oils, none of which formed a picrate. In an experiment using phosphorus trichloride as solvent, similar results were achieved and an attempted cyclodehydrogenation with anhydrous aluminium chloride in dry pyridine yielded unchanged 3:4-benzphenanthrene.

Ultra-Violet Absorption Spectra.

Due to the close structural relationship existing between 3:4-benzphenanthrene and 2:13-benzfluoranthene, it is of interest to compare the ultra-violet absorption spectra of the two compounds.

The spectra were determined with a Unicam spectrophotometer, using cells of fused quartz and are reproduced overleaf. The wavelengths of the more prominent maxima in Angstrom Units are detailed below.

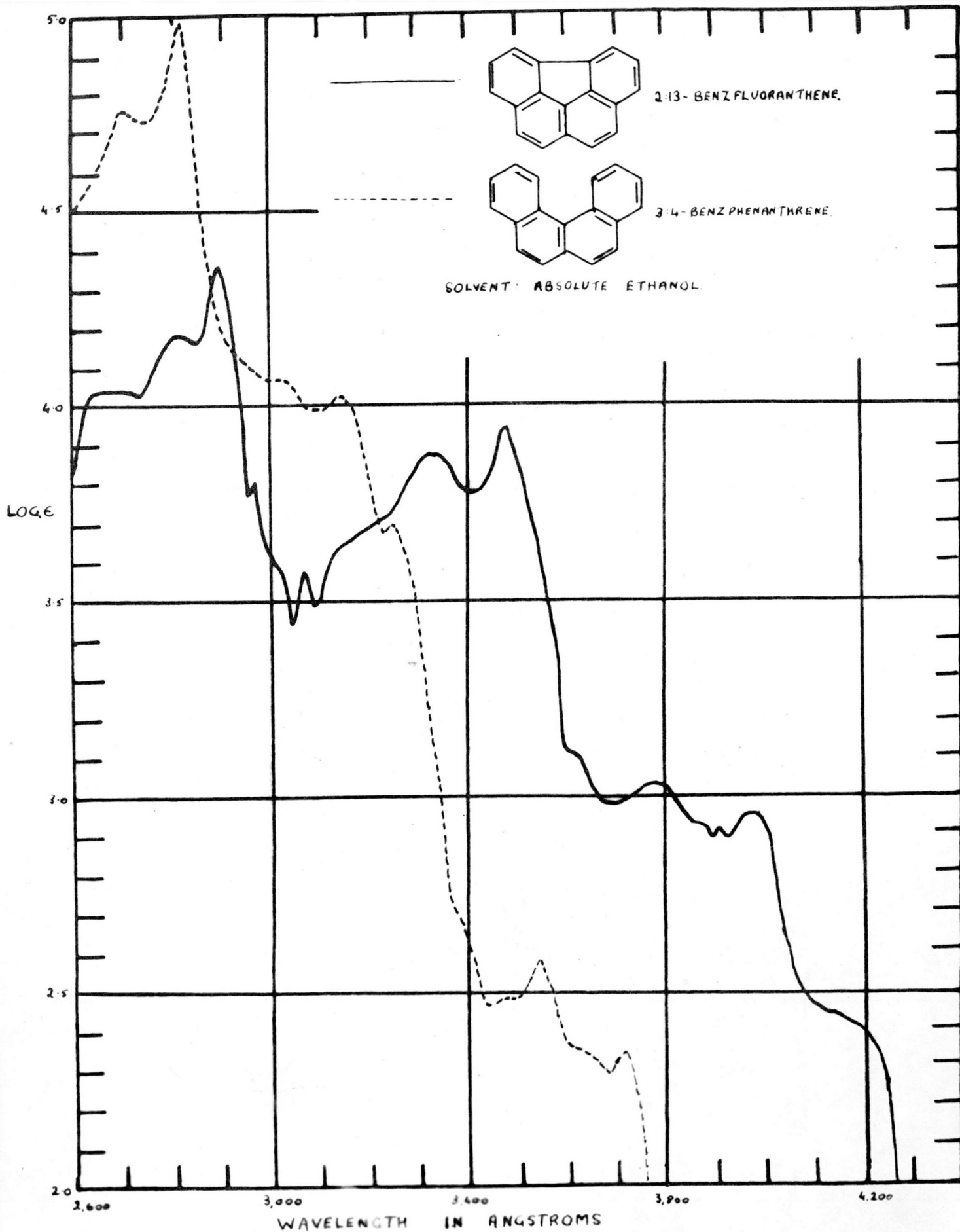
3:4-Benzphenanthrene

2,690
2,810
3,010
3,140
3,250
3,540
3,710

2:13-Benzfluoranthene

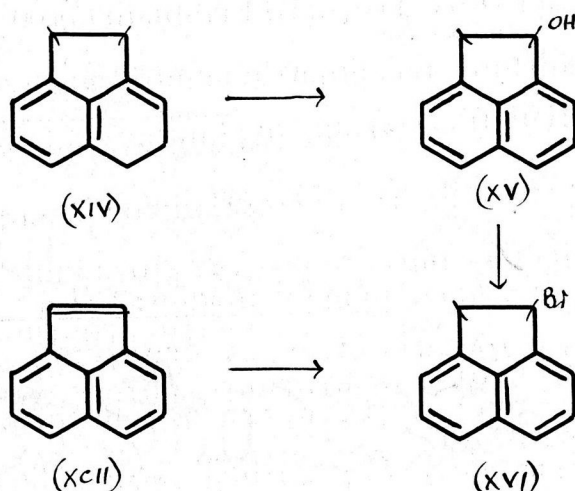
2,810
2,890
3,060
3,330
3,470
3,770
3,970

As expected, the increased conjugation due to the introduction of the bond between the 4' and 5 positions of the 3:4-benzphenanthrene molecule resulted in a bathochromic shift. It may also be noted that 2:13-benzfluoranthene has a larger absorbance than 3:4-benzphenanthrene in the longer wavelengths and a smaller absorbance in the shorter wavelengths.



APPENDIX.The Hydrobromination of Acenaphthylene.

As pointed out on p. 36, the preparation of 1-bromoacenaphthene (XVI), an intermediate in Bachmann's synthesis of 4:5-methylenepheneanthrene, involves the oxidation of acenaphthene (XIV) to the alcohol (XV), which is one of the longer stages in the synthesis.



Comment has already been made on the advantages of preparing 1-bromoacenaphthene by the hydrobromination of acenaphthylene (XCII), but since 1-bromoacenaphthene, prepared by this simple method has been used in several condensation reactions, it is pertinent to summarise the results here. Where possible, comparison is made between the yields obtained by the various methods of preparing 1-bromoacenaphthene as reflected in the yields of subsequent condensation products.

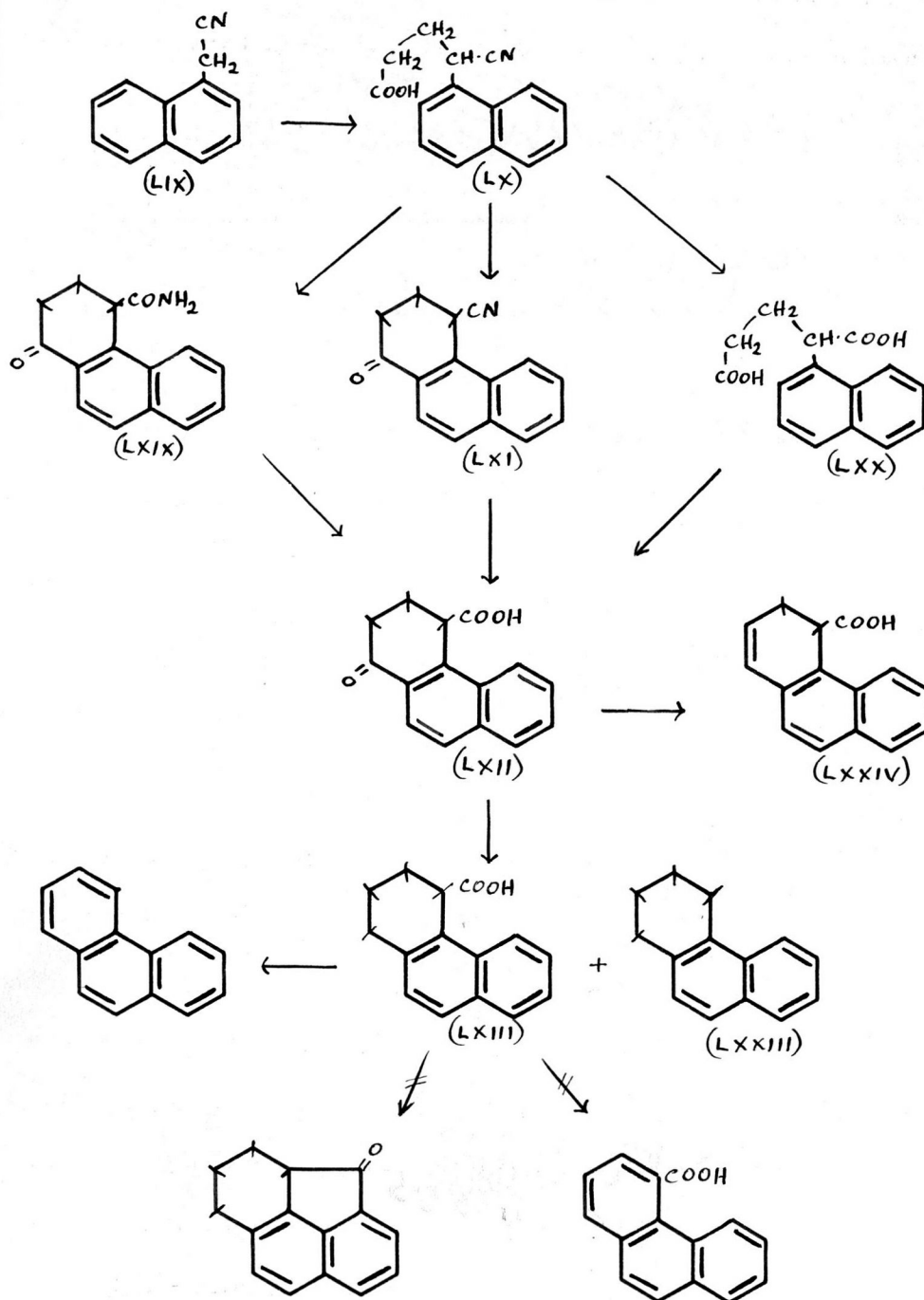
Condensing Agent	with 1-Bromoacenaphthene prepared from		
	Acenaphthenol	Acenaphthene (N.B.S.)	Acenaphthylene
Diethyl malonate	82% (a)	50% (b)	88%
Ethyl acetoacetate	60% (c)	-----	60%
Diethyl methylmalonate	30% (d)	-----	29% (d)

- a) cf. Bachmann and Sheehan (4). The yield of 1-acenaphthenylmalonic acid based on acenaphthene is 53%.
- b) cf. Julia (44).
- c) cf. Campbell, Corrigan and Campbell (29). The condensation was actually carried out with 1-chloroacenaphthene. The yield of 1-acenaphthenylacetoacetate based on acenaphthene is 40%.
- d) The yield of crude product in each case was of the order of 70%.

It is evident from these results that the hydrobromination of acenaphthylene is of value in synthetic work.

EXPERIMENTAL INTRODUCTION.

1. Yields throughout are quoted as the percentages of the theoretical amounts, except where otherwise stated.
2. All melting points were determined on an accurately calibrated Kofler micro apparatus.
3. Fluorescent observations were made under a Hanovia ultra-violet lamp.
4. Chromatographic separations were carried out on B.D.H. chromatographic alumina.
5. Experiments with anhydrous hydrogen fluoride were conducted in the open air in "polythene" apparatus.
6. Analyses were carried out by Drs. Weiler and Strauss, Oxford.

SECTION A.EXPERIMENTAL.ATTEMPTED SYNTHESIS OF 4:5-METHYLENEPHENANTHRENE.(1) A Synthesis from Phenanthrene.

1-Chloromethylnaphthalene.

Reference: Organic Syntheses, Vol.24, p.30

Yield from 256 gm. naphthalene = 185 gm. (52.4%)

b.p. 156-161°/10 m.m.

1-Naphthylacetonitrile (LIX)

Reference: Briggs and Wilson, J.C.S. 1941, 501

Yield from 65 gm. 1-chloromethylnaphthalene = 40 gm.

(64.9%) b.p. 183-4°/12 m.m.

γ-Phenyl-γ-cyanobutyric ester.

(i) To a solution of benzyl cyanide (1.17 gm.) in ethoxyethanol (10 c.c.) containing 11.2 gm. potassium hydroxide per litre was added methyl acrylate (0.86 gm.), and the mixture allowed to stand at room temperature for three hours. Sodium hydroxide (1.5 gm.) in water (5 c.c.) was added to the red-brown solution and the whole boiled under reflux for a further hour, before pouring into water. The clear solution which resulted gave no precipitate on acidification and was extracted with ether. The ethereal extract was washed with sodium carbonate solution and the carbonate washings on acidification deposited a pale brown solid. Crystallisation from water gave colourless plates of phenylacetic acid (m.p. and m.m.p.).

(ii) Benzyl cyanide (5.85 gm.) and methyl acrylate (4.3 gm.) were dissolved in dry pyridine (10 c.c.) and a few drops of a saturated methanolic solution of sodium methoxide added. The solution immediately turned bright red in colour, heat being evolved. On

standing, the colour changed to green but a further addition of sodium methoxide reproduced the red colour, which again reverted to green on standing. This procedure was repeated until the mixture no longer turned green on standing, a permanent reddish brown colour being obtained (6-7 hours). The dark mixture was diluted with ether, washed several times with dilute hydrochloric acid, then with water and dried over sodium sulphate. After removal of the solvent, the dark residue was fractionated under reduced pressure. The desired ester distilled as a colourless oil b.p. $178-181^{\circ}/16$ m.m. (Lit. b.p. = $187-190^{\circ}/18$ m.m.).

Yield = 2.04 gm. (20.1%).

γ :1-Naphthyl- γ -cyanobutyric acid (LX)

To a solution of 1-naphthylacetonitrile (20.50 gm.) and methyl acrylate (10.55 gm.) in dry pyridine (35 c.c.) was added a few drops of a saturated solution of sodium methoxide in methanol. The mixture immediately turned dark red in colour, the temperature rising by some twenty centigrade degrees. The colour slowly changed to green, but on the addition of sodium methoxide solution the colour reverted to red, heat again being evolved. The additions of sodium methoxide solution were continued at intervals until no change in colour or temperature was observed. This usually required several days. The dark mixture was diluted with ether and washed several

times with dilute hydrochloric acid and then with water. Extraction of the ethereal layer with 10% aqueous sodium carbonate solution produced a copious precipitate of small colourless hexagonal plates, which was filtered off. Subsequent extractions were also filtered. This insoluble material was dissolved in hot water and acidification precipitated an acidic oil which solidified on trituration with several changes of cold water. Crystallisation from benzene or aqueous acetic acid gave a pinkish crystalline solid. Under the microscope some of the crystals melted at 108-116° and the remainder at 128-134°. A portion of the acid (0.5 gm.) was dissolved in anhydrous benzene (25 c.c.) and the volume reduced to 5 c.c. On cooling, very small colourless crystals separated. Two further crystallisations from anhydrous benzene gave small colourless prisms m.p. 139-140.5°.

Analysis

Found: C = 74.5% H = 5.7% N = 5.6%

$C_{15}H_{13}O_2N$ requires C = 75.3% H = 5.5% N = 5.8%

The bulk of the acid was taken up in ether and re-extracted with sodium carbonate solution. On standing and seeding, colourless hexagonal plates again separated. Attempts to crystallise the salt from water or organic solvents were unsuccessful but a portion, crystallised from 10% aqueous sodium carbonate solution, gave colourless hexagonal plates m.p. 58-61°.

Analysis.

Found: C = 56.3% H = 5.7% N = 4.7%

$C_{15}H_{12}O_2NNa \cdot 3H_2O$ requires C = 56.7% H = 5.8% N = 4.4%

The crystalline material was converted as before to the free acid by acidification of a hot aqueous solution.

The combined alkaline filtrates on acidification gave a dark brown oil which was taken up in ether and extracted with sodium carbonate. Again, on seeding and standing, colourless plates appeared which were filtered off, dissolved in hot water and acidified. By repeating this procedure, a total of 8.34 gm. acid was obtained as a whitish powder.

The ethereal solution containing the neutral fraction from the crude reaction mixture was evaporated to dryness and the dark residual oil dissolved in methanol (50 c.c.). Aqueous sodium hydroxide (10 c.c., 10%) was added and the solution boiled gently under reflux for two hours before pouring into water and acidifying with concentrated hydrochloric acid. The acidic oil so obtained was taken up in ether and extracted with sodium carbonate. Acidification of the colourless plates which precipitated gave 4.19 gm. acid in all. The combined yield of acid (12.53 gm.) was dissolved in anhydrous benzene (300 c.c.) and the volume reduced to 50 c.c. A little charcoal was added and the solution boiled under reflux for 15 minutes before hot filtering. On cooling, the product crystallised

as small prisms m.p. 132-135°.

Total yield = 11.24 gm. (38.3%)

Ring Closures of 8:1-Naphthyl-8-cyanobutyric acid (LX)

(i) Stannic Chloride. To 8:1-naphthyl-8-cyanobutyric acid (1.5 gm.) in dry benzene (15 c.c.) was added phosphorus pentachloride (1.4 gm.) and the mixture was allowed to stand for one hour at room temperature with occasional swirling before warming to ensure complete reaction. The clear solution was evaporated to dryness under reduced pressure, the residual oil dissolved in dry benzene (15 c.c.), and the solution cooled to 0°C. Stannic chloride (1.6 c.c.) was added and the mixture darkened although no complex separated nor were fumes of hydrogen chloride evolved in any quantity. After one hour at room temperature, the mixture was treated with ice and concentrated hydrochloric acid, and extracted with ether. The ethereal extract was washed successively with water, 10% aqueous sodium carbonate solution and again with water before drying and removal of the solvent. A pale brown solid (0.61 gm.) remained which could not be crystallised from the usual organic solvents. Attempts to form a dinitrophenylhydrazone met with no success.

Acidification of the alkaline washings gave 0.71 gm. unchanged acid (m.p. and m.m.p.). In further experiments, the reaction was allowed to proceed for four hours and twenty hours, but in each case a neutral, non-ketonic product was obtained,

accompanied by much unchanged acid.

(ii) Aluminium Chloride. To a suspension of 8:1-naphthyl-8-cyanobutyric acid (5.13 gm.) in anhydrous benzene (20 c.c.) was added an excess of thionyl chloride, and the mixture was allowed to stand at room temperature for one hour, when most of the acid had dissolved. The solution was boiled for a few minutes and the solvent evaporated under reduced pressure, co-distillation with dry benzene removing the last traces of thionyl chloride. The residual dark oil was dissolved in dry nitrobenzene (70 c.c.) and finely powdered aluminium chloride (7.2 gm.) added with external cooling. After standing at room temperature for two hours, the dark mixture was decomposed with ice and concentrated hydrochloric acid and the nitrobenzene removed by steam distillation. The dark residue was taken up in ether and the extract washed with water, sodium carbonate solution and again with water. Acidification of the carbonate washings precipitated a little dark oil which was discarded. The dried ethereal layer on evaporation gave a dark solid, crystallisation of which from methanol (charcoal) afforded pale brown crystals of 1-keto-4-cyano-1:2:3:4-tetrahydro-phenanthrene (LXI). A portion further crystallised from methanol yielded colourless prisms m.p. 138-139.5°C.

Analysis.

Found: C = 80.7% H = 5.0% N = 6.4%
 $C_{15}H_{11}ON$ requires C = 81.4% H = 5.0% N = 6.3%

65.

The dinitrophenylhydrazone crystallised from dioxan in very small orange needles m.p. 199-201°C.(d).

Analysis.

Found: N = 16.4%

$C_{21}H_{15}O_4N_5$ requires N = 17.5%

Yield = 1.84 gm. (38.8%) m.p. 133-138°C.

(iii) Anhydrous Hydrofluoric acid. A solution of 8:1-naphthyl-8-cyanobutyric acid (10.0 gm.) in anhydrous hydrofluoric acid (500 c.c.) was covered up for 24 hours and the solution allowed to evaporate overnight. A lustrous pale brown crystalline solid remained m.p. 220-236° which was sparingly soluble in ether. The crude product was ground up and digested on the steam bath with 10% aqueous sodium carbonate solution for one hour. On filtration and acidification, no acidic material separated. The crude ketone was crystallised repeatedly from alcohol and a sample of 1-keto-4-carbamoyl-1:2:3:4-tetrahydro-phenanthrene (LXIX) was obtained as pinkish prisms m.p. 234-236°C.

Analysis.

Found: C = 75.5% H = 5.6% N = 5.9% M.Wt. = 249

$C_{15}H_{11}ON$ requires C = 81.4% H = 5.0% N = 6.3% M.Wt. = 221

$C_{15}H_{13}O_2N$ requires C = 75.3% H = 5.5% N = 5.9% M.Wt. = 239

The dinitrophenylhydrazone crystallised as red needles from glacialacetic acid m.p. 310-312°.

Although the melting point was quite sharp, the analysis showed the presence of impurity.

Analysis.

Found: N = 13.8%

 $C_{21}H_{17}O_5N_5$ requires N = 16.7%

Yield of crude ketone 9.50 gm. (95%)

 α :1-Naphthylglutaric acid. (LXX)

A solution of γ :1-naphthyl- γ -cyanobutyric acid (23.0 gm.) in a mixture of glacial acetic acid (50 c.c.) concentrated sulphuric acid (50 c.c.) and water (50 c.c.) was boiled under reflux for four hours, cooled and poured into water. The ethereal extract was well washed with water and then with 10% aqueous sodium carbonate solution. Acidification of the carbonate washings gave the product as a colourless solid m.p. 121-123°C (Lit. m.p. = 122-124°C).

Yield = 23.4 gm. (92.4%)

1-Keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene. (LXII)

(i) A solution of 1-keto-4-cyano-1:2:3:4-tetrahydrophenanthrene (3.38 gm.) in a mixture of glacial acetic acid (100 c.c.), concentrated sulphuric acid (25 c.c.) and water (25 c.c.) was boiled under reflux for two hours. After cooling and pouring into water, the precipitated solid was taken up in ether, and the solution washed with water followed by 10% aqueous sodium carbonate solution. The alkali washings were treated with charcoal, filtered and acidified. The colourless solid so precipitated m.p. 193-197°C(d) crystallised from alcohol or benzene as colourless rhombic prisms m.p. 198-200°C. A mixed melting point determination with authentic 1-keto-4-carboxy-1:2:3:4-tetrahydro-

phenanthrene showed no depression.

Yield = 3.11 gm. (86.7%)

(ii) A solution of 1-keto-4-carbamoyl-1:2:3:4-tetrahydrophenanthrene (6.1 gm.) in a mixture of glacial acetic acid (30 c.c.) concentrated sulphuric acid (30 c.c.) and water (30 c.c.) was boiled under reflux for four hours. The reaction mixture was treated as in the preceding experiment, yielding colourless acidic material m.p. 187-203°.

Crystallisation from benzene gave rhombic prisms m.p. 195-203°. A mixed melting point determination with authentic keto acid gave a doubtful result.

Analysis.

Found: C = 75.0% H = 4.9%

$C_{15}H_{12}O_3$ requires C = 75.0% H = 5.0%

The methyl ester crystallised from methanol as colourless blades m.p. 155-157°. A mixed melting point determination with methyl ester prepared from authentic keto acid showed no depression.

Analysis.

Found: C = 75.2% H = 5.5%

$C_{16}H_{14}O_3$ requires C = 75.6% H = 5.6%

The 2:4-dinitrophenylhydrazone crystallised from glacial acetic acid as very small crimson needles m.p. 277-279°C (d).

Analysis.

Found: N = 12.9%

$C_{21}H_{16}O_6N_4$ requires N = 13.3%

(iii) Reference: Ansell and Hey: J.C.S. 1950, 2874.

α :1-Naphthylglutaric acid (10 gm.) was dissolved in anhydrous hydrofluoric acid (200 c.c.) and the vessel was covered up overnight before allowing the solution to evaporate slowly. The residue was dissolved in aqueous sodium carbonate solution and washed with ether. Acidification of the alkaline layer gave the colourless product which crystallised from benzene as rhombic prisms m.p. 195-8°C.

Yield = 6.5 gm.

A further 1.55 gm. material m.p. 194-7° was obtained from the filtrate.

Total yield = 8.05 gm. (86.5%)

Reduction of 1-Keto-4-carboxy-1:2:3:4-tetrahydro-phenanthrene. (LXII).

(1) cf. Bachmann and Struve: J.Org.Chem. 4, 472 (1939)

1-Keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene (3.0 gm.) was boiled under reflux for twentyfour hours with zinc amalgam (prepared from 20 gm. zinc and 12 gm. mercuric chloride) in glacial acetic acid (30 c.c.), concentrated hydrochloric acid (30 c.c.) and toluene (30 c.c.). A further 15 c.c. of concentrated hydrochloric acid was added in portions at intervals. The mixture was cooled, decanted from the amalgam and well shaken with ether. The organic layer was separated and washed with water followed by aqueous sodium carbonate solution. Acidification of the alkaline washings gave a colourless oil which solidified on trituration with methanol. Attempts

to crystallise the crude product (2.55 gm., m.p. 120-130°C) were unsuccessful.

Lit. m.p. of tetrahydro acid = 145°C.

(ii) cf. Plattner, Furst and Keller: Helv. 32, 2464 (1949)

1-Keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene (1.0 gm.) was dissolved in glacial acetic acid (30 c.c.) containing concentrated hydrochloric acid (1.0 c.c.) and shaken with platinic oxide (10 mg.) under one atmosphere of hydrogen for two hours. Little or no fall in pressure was observed. After filtering off the catalyst, the solution was diluted with water and extracted with ether. The ethereal layer was washed with water and sodium carbonate solution. Acidification precipitated colourless acidic material which was shown to be unchanged starting material (m.p. and m.m.p.).

(iii) cf. Papa, Schwenk and Whitman: J.Org.Chem. 7, 587 (1942)

1-Keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene (0.5 gm.) was dissolved in a 10% aqueous sodium hydroxide solution (25 c.c.) and the temperature raised to 90°C. Nickel-aluminium alloy (0.25 gm.) was added in small portions with mechanical stirring. When the addition of alloy was complete, the temperature was maintained at 90°C for one hour and the suspension filtered hot. On pouring the filtrate into concentrated hydrochloric acid, an oil separated which quickly solidified. This was dried

and boiled under reflux with light petroleum (b.p. 60-80°) containing a little benzene, and hot filtered. The residue melted at 170-185°. A fine precipitate separated from the filtrate m.p. 165-175°. The desired product was thus not obtained.

(iv) Reference: Ansell and Hey: J.C.S. 1948, 2878.

1-Keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene (1.2 gm.), potassium hydroxide (0.95 gm.), hydrazine hydrate (1.0 c.c., 90%) and diethylene glycol (7.5 c.c.) were boiled under reflux for one and a half hours. The condenser was removed and the solution distilled until an internal temperature of 195° was attained, then boiled under reflux for a further four hours. The cold dark solution was diluted with water (15 c.c.) and poured into 6N hydrochloric acid (10 c.c.). The resulting oil was dissolved in ether and extracted with sodium carbonate solution. Evaporation of the dried (sodium sulphate) organic layer gave 0.23 gm. 1:2:3:4-tetrahydrophenanthrene as a brownish oil (25.3%). The picrate crystallised from alcohol in deep yellow needles m.p. 110-111°. (Lit. m.p. 110-112°).

Acidification of the alkaline washings precipitated an oil which solidified on trituration. Crystallisation of the crude product from light petroleum (b.p. 60-80°) containing a little benzene gave 4-carboxy-1:2:3:4-tetrahydrophenanthrene (LXIII) m.p. 143-145°. (Lit. m.p. 145-6°).

Yield = 0.68 gm. (60.2%)

Attempted Ring Closure of 4-Carboxy-1:2:3:4-tetrahydrophenanthrene (LXIII)

4-Carboxy-1:2:3:4-tetrahydrophenanthrene (0.5 gm.) was dissolved in anhydrous hydrofluoric acid (10 c.c.) and the solution covered up overnight. The solid residue obtained on evaporation was dissolved in benzene and washed with water and sodium carbonate solution. Acidification of the alkaline washings gave no unchanged acid. The organic layer was dried over sodium sulphate and the solvent removed leaving a thick oil. This slowly responded to trituration with alcohol to give 0.30 gm. yellow-brown material which gradually fused between 140 and 170°C. Attempts to crystallise the crude product were unsuccessful. No dinitrophenylhydrazone could be prepared.

The crude product (0.25 gm.) was continuously extracted in a Soxhlet apparatus (60 c.c. capacity) for one hour with light petroleum (b.p. 80-100°). The greyish coloured residue melted between 220 and 270°C. Evaporation of the yellow light petroleum extract gave 0.15 gm. material m.p. 125-165°C. This in turn was continuously extracted with ethanol. The pale yellow residue (70 mg.) melted at 180-205°C. Evaporation of the alcoholic solution yielded a yellow amorphous solid (60 mg.) m.p. 100-155°C. Further attempts to crystallise these fractions from the usual solvents were unsuccessful.

The experiment was repeated, the hydrofluoric acid solution being poured onto ice after two hours, and other methods investigated were as follows:-

- (i) Stannic chloride in benzene, overnight at room temperature (on the acid chloride).
- (ii) Anhydrous aluminium chloride in nitrobenzene, $1\frac{1}{2}$ hours at room temperature (on the acid chloride).
- (iii) Anhydrous aluminium chloride in carbon disulphide, 1 hour at 0°C (on the acid chloride).
- (iv) Fusion with aluminium chloride-sodium chloride mixture (cf. Bruce, Sorrie and Thomson: J.C.S. 1953, 2403).
- (v) Polyphosphoric acid (containing 80% phosphorus pentoxide), 30 minutes at 160°C . (cf. Koo: J.A.C.S. 75, 1891 (1953)).

In all cases similar results to the above were obtained. The products had no definite melting points, but melted over wide ranges of temperature. No crystallisation could be effected and attempts to form dinitrophenylhydrazones met with no success, even when the reactants were boiled under reflux for periods up to twelve hours.

Attempted Dehydrogenations of 4-Carboxy-
1:2:3:4-tetrahydrophenanthrene. (LXII)

- (i) A solution of 4-carboxy-1:2:3:4-tetrahydrophenanthrene (0.6 gm.) and chloranil (1.5 gm.) in sulphur free xylene (15 c.c.) was boiled under reflux for nineteen hours. On cooling, the dark mixture

was diluted with ether, filtered and repeatedly extracted with aqueous sodium bicarbonate solution. The combined washings were treated with charcoal and hot filtered. The brown sticky solid obtained on acidification was dissolved in ether and the solution dried and evaporated. The residue, after two crystallisations from aqueous acetic acid, gave colourless crystals (0.25 gm.), shown to be unchanged starting material by m.p. and m.m.p.

The acid free ethereal solution was washed several times with 10% aqueous sodium hydroxide solution, dried and evaporated. The dark oil so obtained was dissolved in a little benzene and adsorbed onto a column of alumina 1 x 20 cm. Development with light petroleum (b.p. 60-80°) produced a band showing a strong blue fluorescence in ultra-violet light, which was eluted with the same solvent and the solution evaporated to dryness. The residual white solid crystallised from ethanol in colourless plates and was identified as phenanthrene (m.p. and m.m.p.). Further elution of the column gave various oils which failed to crystallise or to form picrates.

(ii) A solution of 4-carboxy-1:2:3:4-tetrahydro-phenanthrene (0.5 gm.) and chloranil (1.5 gm.) in nitrobenzene (15 c.c.) was boiled under reflux for two hours. The crude mixture was treated as in the preceding experiment. Acidification of the bicarbonate

washings yielded no acidic material. The neutral fraction was steam distilled to remove nitrobenzene (some colourless plates appearing in the distillate) and the residual oil purified chromatographically, giving phenanthrene (0.19 gm.) which was identified by m.p. and m.m.p.

(iii) An attempted dehydrogenation by the N-bromo-succinimide method of Barnes (J.A.C.S. 70, 145 (1948)) was unsuccessful.

4-Carboxy-3:4-dihydrophenanthrene (LXXIV).

A solution of 1-keto-4-carboxy-1:2:3:4-tetrahydrophenanthrene methyl ester (0.65 gm.) and aluminium isopropoxide (0.6 gm.) in dry isopropyl alcohol (25 c.c.) was simultaneously boiled under reflux and distilled at a rate of two drops per minute. After three hours, no more acetone was detected in the distillate and the mixture was boiled under reflux for thirty minutes. The completeness of reaction was shown by the absence of acetone in the first few drops of distillate. The reaction mixture was cooled, acidified with dilute hydrochloric acid and the oil taken up in ether. Evaporation of the dried ethereal solution gave a clear brownish oil which failed to crystallise on trituration with methanol or light petroleum (b.p. 60-80°). The oil was boiled under reflux with formic acid (20 c.c., 90%) on an oil bath at 145°C for one hour. After taking the volume to 10 c.c. the mixture was cooled and poured into water.

A sticky solid separated which was taken up in ether, dried and the solvent removed. A brownish syrup remained which decolourised dilute permanganate solution but which failed to crystallise. The syrup was dissolved in benzene and adsorbed onto a column of alumina 15 x 1.5 cm. and developed with a 1:1 mixture of benzene and light petroleum (b.p. 60-80°). Two main fractions were eluted.

A. A band showing blue fluorescence in ultra-violet light was eluted with the mixed solvents and evaporation of the solution gave a clear yellow oil (0.27 gm.). This was dissolved in methanol (3 c.c.), 10% sodium hydroxide solution (1 c.c.) added and the solution boiled briskly under reflux for three hours. The hydrolysis mixture was acidified and poured into water. The resulting oil was taken up in ether and extracted with sodium carbonate. Acidification of the carbonate washings gave an oil which solidified on trituration. Crystallisation from alcohol followed by two crystallisations from light petroleum (b.p. 60-80°) gave 70 mg. short colourless rods m.p. 138-140° (unsharp).

Analysis.

Found: C = 79.8% H = 5.6%

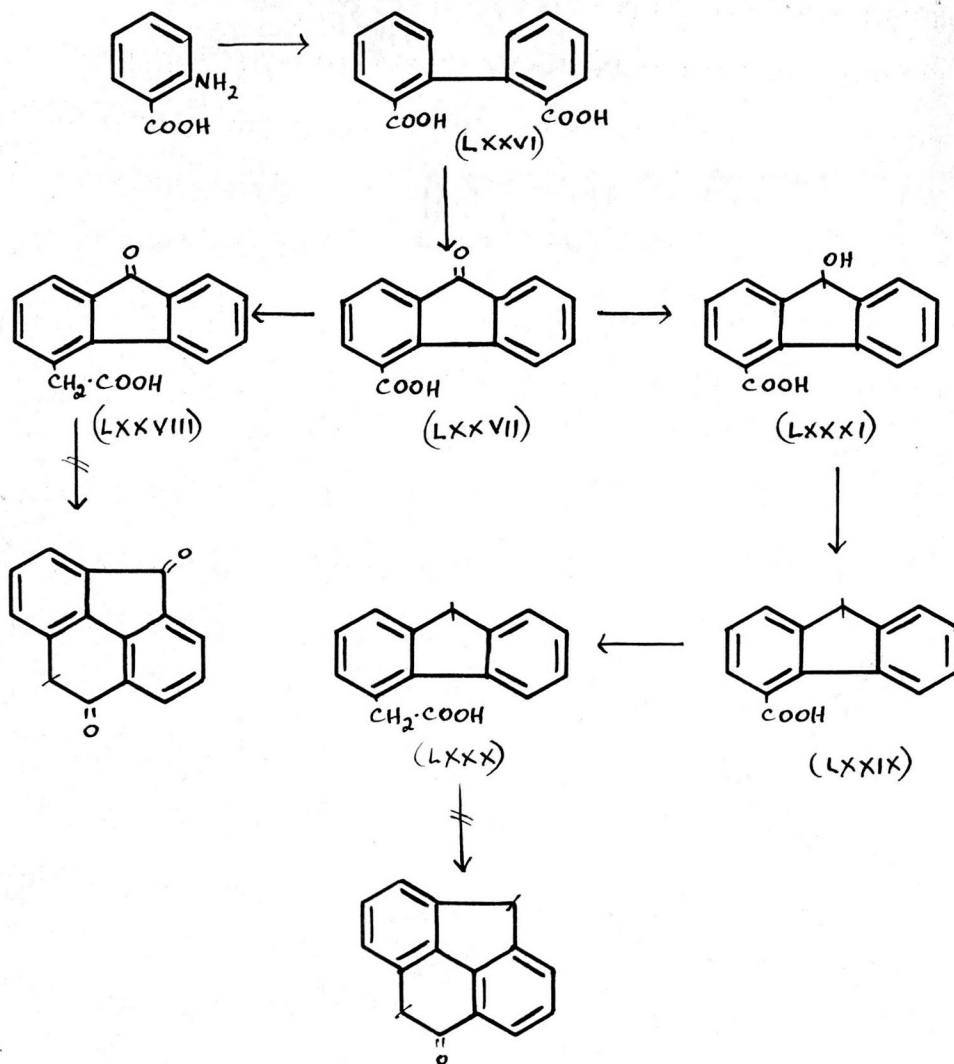
$C_{15}H_{12}O_2$ requires C = 80.3% H = 5.4%

B. Elution with benzene gave an eluate with purplish blue fluorescence under ultra-violet light. Evaporation yielded a clear yellow oil (0.11 gm.)

which was hydrolysed as above. Acidification of the alkaline extract produced a cloudiness which cleared on standing to give a small amount of yellow-brown plates m.p. 127-133°. Attempts to crystallise proved unsuccessful.

SECTION A.

(ii) Synthesis of 4:5-Methylenephenanthrene from Fluorene.



Diphenic acid. (LXXVI)

Reference: Organic Syntheses, Collective Volume I, p. 222

Yield from 100 gm. anthranilic acid = 75.6 gm. (85.6%).

Small tan coloured plates m.p. 234-8° (Lit. m.p. 228-9°).

Fluorenone-4-carboxylic acid. (LXXVII).

Reference: Bischoff and Adams: J.A.C.S. 45, 1030 (1923).

Diphenic acid was cyclised in concentrated sulphuric acid. The crude product crystallised from glacial acetic acid as small yellow needles m.p. 223-5° (Lit. m.p. 227°).

Crude yield from 75 gm. diphenic acid = 63 gm. (90.7%)

Fluorenone-4-acetic acid. (LXXVIII)

Reference: Bachmann and Sheehan: J.A.C.S. 62, 2687 (1940)

The Arndt-Eistert reaction was carried out on 10 gm. fluorenone-4-carboxylic acid. The product, methyl fluorenone-4-acetate, was obtained as a brown crystalline solid m.p. 120-134°. Two crystallisations from methanol raised the melting point to 133-136° (Lit. m.p. 134-5°). Hydrolysis of the purified ester gave the acid which crystallised from ethanol as yellow needles m.p. 199-203° (Lit. m.p. 204-206°).

Yield = 4.2 gm. (39.5%)

Fluorenone-4-carboxylic acid. (LXXXI).

Fluorenone-4-carboxylic acid was reduced with zinc in boiling sodium hydroxide solution and the product crystallised from benzene. Small colourless needles m.p. 198-201°. (Lit. m.p. 202-203°).

Yield from 13.0 gm. fluorenone acid = 10.8 gm. (82.3%)

Fluorene-4-carboxylic acid (LXXIX).

Fluorenol-4-carboxylic acid was reduced with hydriodic acid. Crystallisation from benzene gave small colourless needles m.p. 190-192°. (Lit. m.p. 189-191°). Yield from 18.0 gm. fluorenol acid = 12.0 gm. (67%).

Fluorene-4-acetic acid (LXXX).

The crude acid from the Arndt-Eistert reaction was twice crystallised from benzene and was obtained as a felt of colourless needles m.p. 173-6°. (Lit. m.p. 178-9°).

Yield from 9.0 gm. fluorene-4-carboxylic acid = 4.8 gm. (50.0%).

Attempted Cyclisations of Fluorenone-4-acetic acid. (LXXVIII).

- (i) A solution of fluorenone-4-acetic acid (1.0 gm.) in polyphosphoric acid (20 gm., containing 80% phosphorus pentoxide) was heated at 60° for two hours and poured into water. The ether-chloroform extract was washed with water, sodium carbonate and again with water. Evaporation of the dried (sodium sulphate) organic layer left a trace of solid material. Acidification of the carbonate washings produced a copious yellow precipitate which, after crystallisation from alcohol, was shown to be unchanged starting material (m.p. and m.m.p.).
- (ii) A solution of fluorenone-4-acetic acid (0.5 gm.) in anhydrous hydrofluoric acid (10 c.c.) was covered up and allowed to stand overnight. The residue obtained on evaporation was dissolved in ether-chloroform

solution and treated as in the preceding experiment. Evaporation of the dried organic layer yielded no residue. Acidification of the alkaline washings gave fluorenone-4-acetic acid (m.p. and m.m.p.).

Further attempts were made as follows:-

(iii) Anhydrous aluminium chloride in nitrobenzene for two hours and overnight at room temperature (on the acid chloride).

(iv) Concentrated sulphuric acid, overnight at room temperature and two hours at 100°.

In each case the only product isolated was fluorenone-4-acetic acid.

(v) Fusion with aluminium chloride-sodium chloride mixture, two minutes at 180-200° (cf. Bruce, Sorrie and Thomson: J.C.S. 1953, 2403). Extensive charring occurred. The non-acidic fraction afforded an insignificant amount of amorphous solid and acidification of the alkaline extracts only a trace of acidic material.

Attempted Cyclisations of Fluorene-4-acetic acid (LXXX).

(1) Phosphorus pentachloride (0.5 gm.) and fluorene-4-acetic acid (0.5 gm.) were suspended in dry benzene (20 c.c.) and the mixture allowed to stand at room temperature for one hour before warming to ensure complete reaction. The solvent was removed under reduced pressure and the residual acid chloride redissolved in dry nitrobenzene (20 c.c.). Finely ground aluminium chloride (0.6 gm.) was added and

the mixture left overnight at room temperature, before decomposition with ice and concentrated hydrochloric acid. Steam distillation removed the solvent and the dark oily residue was extracted into ether-chloroform and the solution washed with water, aqueous sodium carbonate solution and again with water. Acidification of the alkaline washings precipitated only a trace of acidic material. The dried (sodium sulphate) organic layer was evaporated and the orange oil which resulted triturated with alcohol. A small amount (0.02 gm.) of brown solid separated (approximate m.p. = 170°) which could not be crystallised and which did not form a dinitro-phenylhydrazone. The trituration liquors were evaporated and the residue dissolved in benzene and adsorbed on a short column of alumina. Development and elution with benzene gave a fraction showing a green fluorescence under ultra-violet light which on evaporation yielded a few mgms. of a yellow oil. This failed to crystallise or yield a dinitrophenylhydrazone. Elution of the column with alcohol gave a fraction which on evaporation yielded a minute amount of orange solid.

Further attempts were made as follows:-

- (ii) Polyphosphoric acid (80% phosphorus pentoxide) 160° for fortyfive minutes.
- (iii) Anhydrous hydrofluoric acid overnight.

In these experiments, appreciable quantities of impure fluorene-4-acetic acid were obtained along

with non-acidic mixtures. Attempts to separate and purify these non-acidic fractions by chromatography and crystallisation met with no success. In no case could a dinitrophenylhydrazone derivative be formed. (iv) Attempted cyclisations in cold concentrated sulphuric acid overnight and for two hours resulted in the formation of water soluble products.

SECTION A.

(iii) Syntheses of 4:5-Methylenephenanthrene from Acenaphthene.

a) Experiments with 1-Acenaphthenone.

1-Acenaphthenol

Reference: Fieser and Cason: J.A.C.S. 62, 432 (1940)

Acenaphthene was oxidised by the lead tetra-acetate method and the resulting acenaphthenyl acetate purified by distillation (b.p. 128-130°/0.5 m.m.) before hydrolysis with methanolic sodium hydroxide. Crystallisation from benzene gave the product as a felt of fine colourless needles m.p. 145-6° (Lit. m.p. 144.5-145.5°).

Yield from 154 gm. acenaphthene = 115 gm. (67.7%).

1-Acenaphthenone

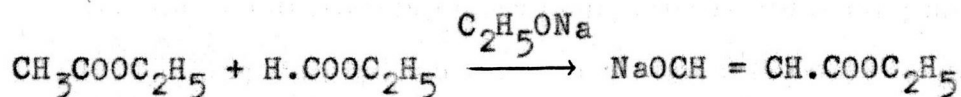
Acenaphthenol was oxidised with chromic acid in glacial acetic acid and the crude ketone purified by steam distillation followed by crystallisation from benzene-light petroleum (b.p. 60-80°).

Yield from 45 gm. acenaphthenol = 26.9 gm. (60.6%).

Ethyl sodium formylacetate.

References: Cogan: Bull.Soc.Chim. 8, 125 (1941)

McElvain and Clarke: J.A.C.S. 69, 2657
(1947)



Yield from 44 gm. ethyl acetate = 45 gm. (65.2%)

Attempted Condensation of Ethyl sodium formylacetate
and 1-acenaphthenone.

(i) cf. Henderson: Thesis, (Edin.), p.118.

Acenaphthenone (0.5 gm.) was dissolved in warm alcohol (15 c.c.) and when the temperature had fallen to 40°, ethyl sodium formylacetate (0.65 gm.) was added. The deep violet coloured solution was stoppered up and allowed to stand at room temperature for two hours with intermittent shaking. The yellow precipitate which had formed, when crystallised from benzene, afforded yellow needles (0.28 gm.) which were shown to be biacenaphthylidenone (m.p. and m.m.p.). The experiment was repeated at 25° with the same result.

(ii) Ethyl sodium formylacetate (0.65 gm.) was added to a solution of acenaphthenone (0.5 gm.) in cold methylene chloride (5 c.c.), a deep violet colour developing immediately. The passage of dry hydrogen chloride gas discharged the colour and precipitated sodium chloride from the reaction mixture which was stoppered up and allowed to stand at room temperature for one hour with occasional shaking. The solid material was filtered off and extracted several times with boiling benzene. The filtrates on

cooling deposited a total of 0.11 gm. biacenaphthylidenone (m.p. and m.m.p.)

Diethyl Acetal.

Reference: Organic Syntheses, Collective Volume I, 1.

The product was twice fractionated on a column of indented glass and was obtained as a colourless oil b.p. 102-104° (Lit. b.p. 101-103.5°).

Yield from 100 gm. acetaldehyde = 93.5 gm. (41.1%).

Bromoacetal.

Reference: Hartung and Adkins: J.A.C.S. 49, 2517 (1927).

The product was obtained as a pale yellow oil b.p. 165-170° (Lit. b.p. 167-178°).

Yield from 93.5 gm. acetal = 50 gm. (32.0%).

Cyanoacetal.

The product was purified by steam distillation and distilled under reduced pressure. A colourless oil b.p. 39-44°/3 m.m. (Lit. b.p. 52-54 /5 m.m.).

Yield from 50 gm. bromoacetal = 31 gm. (85.4%).

Attempted Condensation of Cyanoacetal and 1-Acenaphthenone.

cf. Henderson: Thesis, (Edin.), p. 118.

(i) Acenaphthenone (0.5 gm.) and cyanoacetal (0.43 gm.) were dissolved in hot ethanol (15 c.c.) and the colourless solution cooled to 40°. The addition of 10% aqueous sodium hydroxide solution (2 c.c.) produced an immediate deep red colouration. On scratching, a yellow solid began to separate out and after standing at room temperature for thirty

minutes, the mixture was filtered. Crystallisation of the solid from benzene gave bright yellow needles (0.15 gm.) of biacenaphthylidenone (m.p. and m.m.p.). The filtrate on standing overnight deposited a further 0.25 gm. of the same material.

The experiment was repeated at 25° with the same result.

(ii) A solution of acenaphthenone (0.5 gm.) cyanoacetal (0.43 gm.) and piperidine (0.1 c.c.) in glacial acetic acid (10 c.c.) was gently boiled under reflux for ninety minutes. The very dark solution on cooling deposited some dark material (0.13 gm.) which was filtered off but which could not be purified. The filtrate on pouring into water gave a black sticky oil which failed to solidify.

The experiment was repeated with a reflux period of fortyfive minutes and, although very little solid material separated on cooling, the same sticky oil was obtained when the mixture was poured into water.

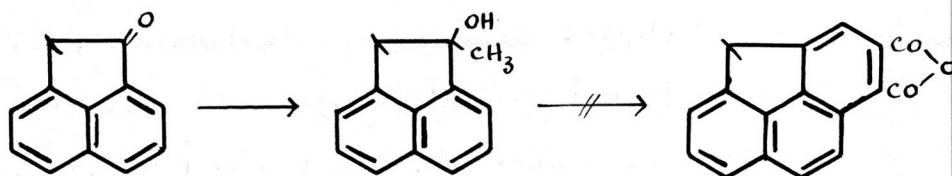
In a further attempt, the reactants were allowed to stand at room temperature for twentyfour hours. Dilution with water gave 0.43 gm. acenaphthenone (m.p. and m.m.p.).

(iii) Acenaphthenone (0.5 gm.) and cyanoacetal (0.43 gm.) were dissolved in methylene chloride (5 c.c.) and the solution saturated with dry hydrogen chloride gas. The colour changed rapidly to deep red and on standing overnight, a black solid had separated which

was filtered off and repeatedly extracted with hot benzene. The filtrates on cooling yielded 0.28 gm. biacenaphthylidenone (m.p. and m.m.p.).

Attempted Diels-Alder reaction
with 1-Hydroxy-1-methylacenaphthene.

Reference: Brown and Hammick: J.C.S., 1948, 1397.



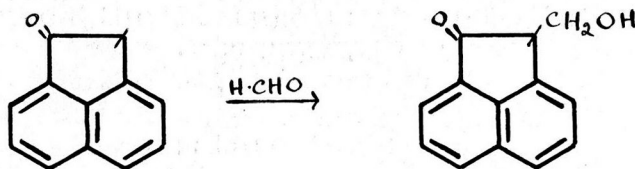
Acenaphthenone (2.1 gm.) in ice-cold dry benzene (20 c.c.) was added to a suspension of methylmagnesium iodide (prepared from 2.11 gm. methyl iodide and 0.36 gm. magnesium) in anhydrous ether (15 c.c.) The mixture was decomposed, washed and the ethereal layer dried over sodium sulphate. Evaporation under reduced pressure at 40° gave a crystalline mass to which was added maleic anhydride (2.45 gm.) and acetic anhydride (25 c.c.). The pale yellow solution was boiled under reflux for twentyfour hours and cooled. No solid material separated but on decomposing the acetic anhydride with water, a brown amorphous powder was precipitated (0.4 gm.) which could not be crystallised. The powder was intimately mixed with ten times its bulk of calcium oxide and heated to a dull redness. A heavy yellow vapour condensed on the upper part of the tube to give a red oil which was dissolved in benzene and

adsorbed onto a column of alumina 1 x 20 cm. Development with light petroleum (b.p. 60-80°) and evaporation of the various eluates gave a series of oils all of which failed to give picrates.

In one experiment, maleic anhydride (1.23 gm.) in a few c.c.s. of dry ether was added to a dried (sodium sulphate) solution of 1-hydroxy-1-methyl-acenaphthene (prepared from 2.1 gm. acenaphthenone) and the mixture allowed to stand for one hour at room temperature before evaporating to dryness on the steambath. The residual brown oil was triturated with alcohol and the solid material so obtained filtered off. Crystallisation from benzene gave golden yellow needles (0.4 gm.) of biacenaphthylidenone (m.p. and m.m.p.).

1-Hydroxymethyl-2-Acenaphthenone.

Reference: Gault and Kalopissis: *Compt. Rend.* 229, 624 (1949)
Gault: Private communication.



To a suspension of acenaphthenone (6.0 gm.) in a cold aqueous saturated solution of barium hydroxide (100 c.c.), was added, in small portions, an aqueous solution of formaldehyde (3.3 c.c., 30% by volume) with continuous agitation. The mixture was allowed to stand at room temperature with occasional shaking

for one hour, a pink colour developing, then stoppered up and left for twelve hours. After filtration, the solid material was shaken with cold benzene to remove unreacted acenaphthenone, filtered and treated with steam to remove the last traces of starting material.

Recovered acenaphthenone = 2.54 gm.

Yield of ketol = 3.1 gm. (76.4% based on unrecovered acenaphthenone).

The ketol was impure and after crystallisation from alcohol or glacial acetic acid, melted over the range 204-222°. A portion was partially dissolved in alcohol and hot filtered. From the filtrate very small crystals separated m.p. 127-142°. The residue melted at 201-207°. (Lit. m.p. 213-215°). Further crystallisation did not improve the melting point.

In other experiments, the acenaphthenone was previously steam-distilled and passed through a fine sieve to obtain the material in a finely divided state. In one case, mechanical stirring was used throughout. The formalin concentration was checked by thiosulphate titration. In all experiments a highly impure product was obtained.

Bromination of 1-Hydroxymethyl-2-acenaphthenone.

Phosphorus tribromide (0.25 c.c.) was added to a solution of crude 1-hydroxymethylacenaphthenone (1.0 gm.) in hot dry chloroform (170 c.c.). The

solution immediately turned yellow-orange in colour and was allowed to stand at room temperature for one hour before hydrolysis with water. Evaporation of the washed and dried organic layer gave an oil which responded to trituration with methanol giving a bright yellow solid (0.58 gm.) m.p. 191-197°. Crystallisation from glacial acetic acid gave bright orange prisms m.p. 203-4°.

Analysis.

Found: C = 86.0% H = 4.5% M.Wt. = 292

$C_{26}H_{16}O_2$ requires C = 86.7% H = 4.5% M.Wt. = 360

The product contained no bromine, decolourised dilute permanganate solution and failed to give a dinitrophenylhydrazone.

The Reformatsky Reaction on 1-Acenaphthenone.

To a solution of acenaphthenone (10.0 gm.) in a mixture of dry benzene (10 c.c.) and dry toluene (10 c.c.) was added zinc dust (3.9 gm.) which had been previously washed with dilute hydrochloric acid, water, acetone and ether and dried at 95° (Note 1). A solution of ethyl bromoacetate (9.9 gm.) in dry benzene (12.0 c.c.) and dry toluene (12.0 c.c.) was added in portions over a period of thirty minutes, with heating and stirring on the water bath. These additions were accompanied by a brisk effervescence, the reaction mixture turning yellow-green then red in colour. After heating under reflux for a further two hours, most of the zinc had dissolved and an orange gelatinous precipitate had separated. The reaction mixture was decanted from

the unreacted zinc which was washed several times with hot benzene and the whole treated with dilute sulphuric acid. An insoluble yellow solid was filtered off which on crystallisation from benzene, gave 1.1 gm. bright yellow needles m.p. 257-258°. A mixed melting point determination with an authentic specimen of biacenaphthylidenone showed no depression. (Note 2).

The solution of reaction products was washed, dried and evaporated and the oily residue dissolved in methanol (200 c.c.). Aqueous sodium hydroxide solution (20 c.c., 10%) was added and the mixture boiled under reflux for two hours. A precipitate which had separated on the addition of sodium hydroxide solution was filtered off and found to be biacenaphthylidenone (0.5 gm.). Acidification of the methanolic filtrate gave a brown precipitate which was filtered off and washed on the filter with a little water. This caused a yellow substance to separate from the filtrate which on crystallisation from benzene gave 0.2 gm. bright yellow plates m.p. 133-4°. (Note 3).

Analysis.

Found: C = 79.3% H = 4.8%

$C_{14}H_{10}O_2$ requires C = 80.0% H = 4.8%

The methyl ester crystallised from methanol as straw coloured needles m.p. 112-114°.

Analysis.

Found: C = 80.9% H = 5.9%

$C_{15}H_{12}O_2$ requires C = 80.4% H = 5.4%

The brown acid (0.7 gm.) which decomposed on heating above 200° , was purified through the methyl ester. Regeneration gave a buff coloured acid which crystallised from benzene containing a little acetone as very small pale yellow blades m.p. $239-241^{\circ}$ (d).

Analysis.

Found: C = 80.0% H = 4.9%

$C_{14}H_{10}O_2$ requires C = 80.0% H = 4.8%

The methyl ester, crystallised from methanol, gave fine almost colourless needles m.p. $115-116^{\circ}$.

Analysis.

Found: C = 80.5% H = 5.2%

$C_{15}H_{12}O_2$ requires C = 80.4% H = 5.4%

Total yield of crude acids = 0.9 gm. (7.2%) (Note 4).

Notes.

1. Later experiments were carried out with zinc wool which was used without preliminary treatment. The yields of unsaturated acids were improved considerably.
2. The yields of biacenaphthylidenone varied from 10-40%.
3. This separation of the two acids was quite fortuitous and could not be repeated. Subsequently, the hydrolysis mixture was reduced in volume, poured into water and acidified. The ethereal extract was washed with aqueous sodium carbonate and the acids reprecipitated with concentrated hydrochloric acid.
4. The best results were achieved under the following conditions:

5 gm. acenaphthenone in 10 c.c. mixed dry solvents.
20 gm. zinc wool added in lots of 10 gm.
10 c.c. ethyl bromoacetate added in lots of 25 c.c.
at 30 minute intervals.

A total reaction period of four hours under reflux was allowed, stirring being unnecessary.

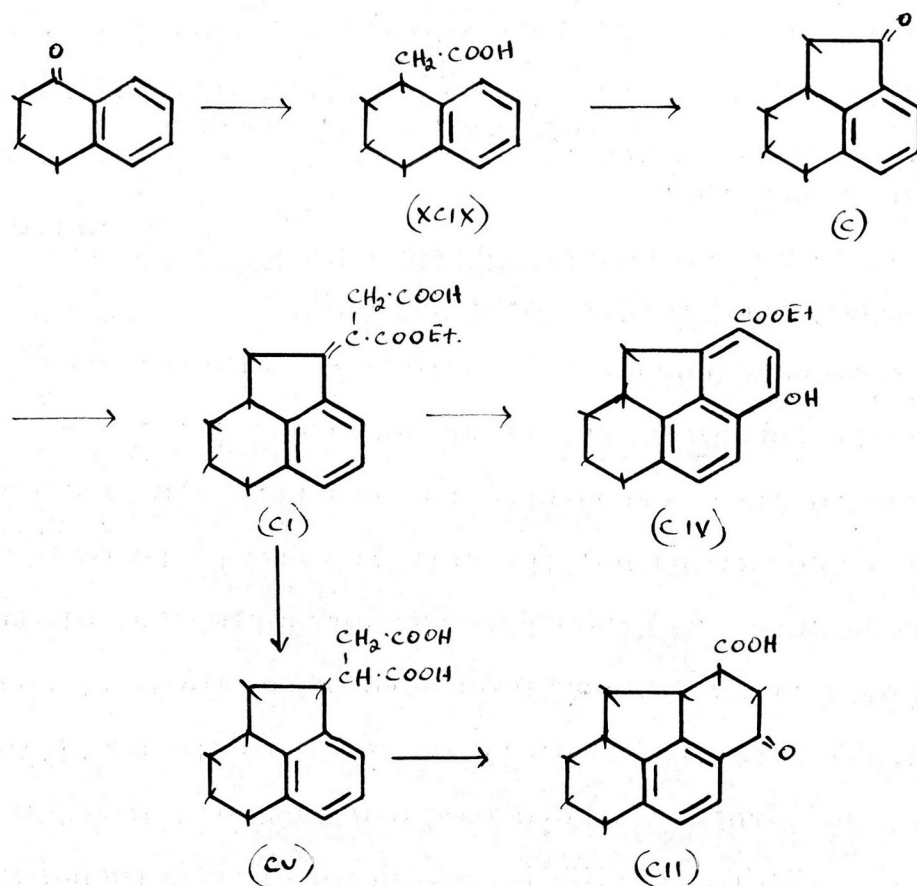
The reaction mixture was decomposed as above and hydrolysed with 50 c.c. 10% aqueous sodium hydroxide solution in 500 c.c. methanol. Treatment of the hydrolysis mixture as in 3 gave 4.8 gm. (76.4%) of crude mixed acids as a brown solid.

Hydrogenation of the Reformatsky Products.

A solution of crude mixed unsaturated acids in dry ethyl acetate (25 c.c.) was shaken with platinic oxide (10 mg.) under one atmosphere of hydrogen at room temperature. When the theoretical amount of hydrogen had been taken up, the catalyst was filtered off and the solution evaporated to dryness. The residual oil on trituration with light petroleum (b.p. 60-80°) afforded a colourless solid which crystallised from aqueous acetic acid m.p. 113-115°. A mixed melting point with authentic 1-acenaphthenylacetic acid gave no depression.

Yield = 0.64 gm. (64%)

b) The Stobbe Condensation with Tetrahydro-1-acenaphthenone.



1:2:3:4-Tetrahydronaphthalene-1-acetic acid (XCIX)

References: Johnson and Glen: J.A.C.S. 71, 1087 (1949)

Bachmann and Cole: J.A.C.S. 62, 832 (1940)

The crude hydroxy ester obtained from the Reformatsky reaction on α -tetralone (30.0 gm.) was dehydrated by boiling under reflux with 90% formic acid. Hydrolysis of the resulting mixture of esters afforded the mixture of crude unsaturated acids (28.25 gm.) as a pale brown solid. Hydrogenation over 5% palladium-charcoal proceeded smoothly under two atmospheres of hydrogen at room temperature, and the

tetrahydronaphthaleneacetic acid was obtained as a clear yellow oil.

Yield = 26.1 gm.

2a:3:4:5-Tetrahydro-1-acenaphthenone (C).

The crude acid obtained above was cyclised overnight in anhydrous hydrogen fluoride and the crude product purified by steam distillation. Crystallisation from light petroleum (b.p. 60-80°) gave colourless prisms m.p. 103-104°. (Lit. m.p. = 102°).

Yield = 20.1 gm. (56.9% based on α -tetralone)

The Stobbe Reaction on 2a:3:4:5-Tetrahydroacenaphthenone.

To a boiling solution of potassium (3.13 gm.) in t-butyl alcohol (75 c.c.) in an atmosphere of dry nitrogen, was added tetrahydroacenaphthenone (12.5 gm.) and diethyl succinate (16.0 gm.). The mixture darkened at once, but after boiling under reflux for forty-five minutes, the solution was pale yellow in colour. A total reaction period of ninety minutes was allowed before the mixture was cooled and acidified with a solution of concentrated hydrochloric acid (20 c.c.) in water (60 c.c.). The solvents were removed under reduced pressure and the oily residue dissolved in ether and washed with aqueous sodium carbonate solution. Acidification of the alkaline washings precipitated the half-ester as a pale yellow oil which was extracted into ether, the solution dried over sodium sulphate and the solvent removed.

Yield of crude half-ester = 15.27 gm.

Analysis. $C_{18}H_{20}H_4$ requires C = 72.0% H = 6.7%

Found: C = 68.3% H = 7.1%

Ring Closure of Half-ester (CI)cf. Fieser and Hershberg: J.A.C.S. 59, 1028 (1937)

(i) A mixture of the half-ester (0.90 gm.) anhydrous zinc chloride (0.10 gm.), acetic anhydride (10 c.c.) and glacial acetic acid (5 c.c.) was gently boiled under reflux in an atmosphere of dry nitrogen for three hours. Water (10 c.c.) was cautiously added followed by concentrated hydrochloric acid (5 c.c.) and the heating continued for a further fortyfive minutes.

The dark red mixture was poured into water, the dark oil so precipitated taken up in ether and the ethereal layer washed with water and sodium carbonate solution. The carbonate extracts, after charcoal treatment, were acidified with concentrated hydrochloric acid. A dark oil was precipitated which partly solidified on standing overnight but which precipitated from organic solvents as an oil. No purification could be effected.

The ethereal layer, after drying over anhydrous sodium sulphate was taken to dryness, yielding a small amount of dark oil which failed to solidify.

(ii) A solution of the half-ester (0.65 gm.) in anhydrous hydrogen fluoride (20 gm.) was covered up for three hours and poured onto ice. A sticky brown solid was obtained which was extracted with an ether-chloroform mixture and well washed with water and then

with 10% aqueous sodium carbonate solution. Acidification of the alkaline washings gave a dark acidic oil which was discarded after attempts at purification.

The organic layer was dried over sodium sulphate and removal of the solvent from the filtered solution afforded a pale brown solid which crystallised from a benzene-alcohol mixture as squat needles m.p. 192-199°. Further crystallisation from the same solvent gave tan coloured needles m.p. 200-202°.

Analysis.

$C_{18}H_{18}O_3$ requires C = 76.6% H = 6.4%

Found: C = 76.3% H = 6.0%

Yield = 50 mg.

Attempts to form a dinitrophenylhydrazone met with no success.

α :1-(2a:3:4:5-Tetrahydroacenaphthenyl)-succinic Acid (CV)

(i) The half-ester (1.7 gm.) was dissolved in 10% aqueous sodium hydroxide solution (50 c.c.) and the solution gently boiled under reflux overnight. The solution was diluted with water (50 c.c.), 4% sodium amalgam (40 gm.) added and the heating continued for twenty hours further. The solution was decanted and after charcoal treatment, acidified with concentrated hydrochloric acid. A pale brown oil (1.54 gm.) separated which could not be crystallised.

(ii) A solution of half-ester (15.3 gm.) in 5% aqueous sodium hydroxide solution (400 c.c.) was gently boiled under reflux overnight, cooled and acidified. The chilled mixture was extracted with ether and the

organic layer dried over sodium sulphate and the solvent removed. The residual brown viscous oil was dissolved in ethyl acetate (250 c.c.), 5% palladium-charcoal catalyst (5.0 gm.) added and the mixture shaken for twelve hours at room temperature under two atmospheres of hydrogen. Semiquantitative measurements showed that the hydrogen uptake amounted to at least 85% of the theoretical amount. The catalyst was removed by filtration and the clear yellow filtrate taken to dryness. A yellowish glass remained which broke up readily to give a whitish powder. This could not be purified by crystallisation, but was assumed to be the tetrahydroacenaphthenylsuccinic acid (CV) and was used directly for the ring closure experiments.

Yield = 12.5 gm.

1-Keto-3-carboxy-1:2:3:4:5:6:7:8-octahydro-
4:5-methylenephenanthrene (CII)

(i) Tetrahydroacenaphthenylsuccinic acid (1.0 gm.) was dissolved in anhydrous hydrogen fluoride (20 gm.). The solution was covered up overnight and then allowed to evaporate slowly. The brown residue was dissolved in aqueous potassium carbonate solution, washed with ether and the acidic material reprecipitated with concentrated hydrochloric acid. The dried precipitate was only partially soluble in ether and was triturated with 20 c.c. of this solvent and filtered. Crystallisation of the residue from alcohol gave 0.28 gm. flat colourless needles m.p. 230-233°. A sample recrystallised

for analysis melted at 233-235°.

Analysis.

Found: C = 74.8% H = 6.4%

$C_{16}H_{16}O_3$ requires C = 75.0% H = 6.3%

The methyl ester crystallised from methanol as colourless rhombic prisms m.p. 153-155° (unsharp).

Analysis.

$C_{17}H_{18}O_3$ requires C = 75.5% H = 6.7%

Found: C = 75.2% H = 6.7%

The dinitrophenylhydrazone was prepared by boiling under reflux for one hour an alcoholic solution of the keto acid and dinitrophenylhydrazine. On adding a few drops of concentrated hydrochloric acid, the derivative separated immediately. Crystallisation from glacial acetic acid gave tiny crimson prisms which charred between 280 and 290°.

Analysis.

$C_{22}H_{20}O_6N_4$ requires N = 12.8%

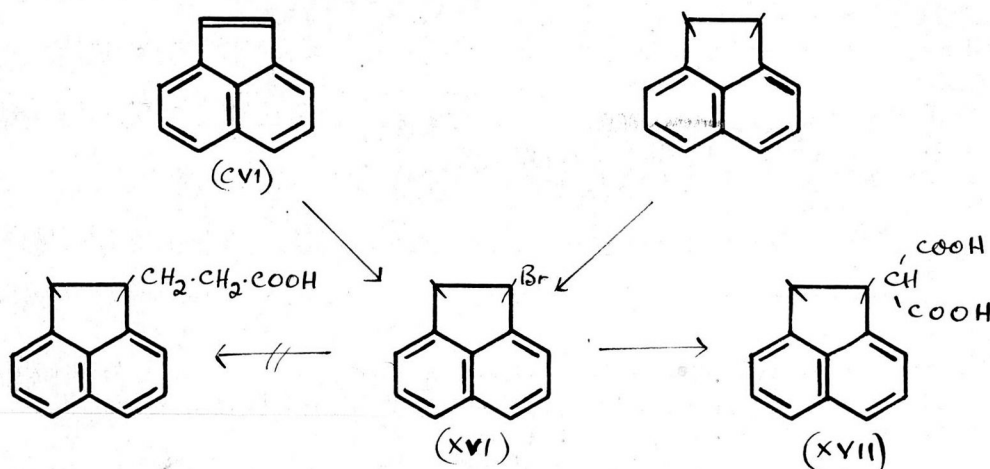
Found: N = 12.8%

The ether soluble fraction was extracted with sodium carbonate solution and the extracts treated with charcoal and acidified. The precipitated oil responded to trituration with cold water and the solid material (0.33 gm.) was filtered off and dried before trituration with ether (3 - 4 c.c.). The residue after two crystallisations from alcohol was obtained as light brown needles m.p. 192-222°. Further crystallisation had little effect on the melting point.

Yield of keto acid m.p. 230-233° = 0.28 gm. (29.5%)

(ii) A solution of tetrahydroacenaphthenylsuccinic acid (2.0 gm.) in 40 gm. polyphosphoric acid (containing 80% phosphorus pentoxide) was heated at 60° for fortyfive minutes and poured into water. The resulting sticky solid was filtered off and triturated with ether (10 c.c.). Crystallisation of the colourless residue gave material of m.p. $183-201^{\circ}$. Further crystallisation from the same solvent gave 65 mg. colourless needles m.p. $187-218^{\circ}$.

c) The Hydrobromination of Acenaphthylene.



1-Bromoacenaphthene (XVI)

(1) Reference: Julia: Bull. Soc. Chim., 1952, 1066.

Acenaphthene (6.2 gm.), N-bromosuccinimide (8.0 gm.) and benzoyl peroxide (50 mg.) in carbon tetrachloride (15 c.c.) were gently boiled under reflux for three hours. On cooling, the succinimide was filtered off and the filtrate evaporated under reduced pressure below 40° . A dark oil was obtained which failed to crystallise on scratching or on trituration with dry light petroleum (b.p. $60-80^{\circ}$).

(ii) A suspension of acenaphthylene (10.0 gm.) in ether (25 c.c.) was saturated with bromine-free hydrogen bromide gas. As the reaction proceeded, the suspended solid dissolved giving finally a clear brown solution which was well washed with water followed by aqueous sodium bicarbonate solution, and dried for several hours over anhydrous sodium sulphate. Evaporation of the filtered solution below 40° gave a pale brown crystalline mass m.p. $65-68^{\circ}$. (Lit. m.p. $70.5-71.5^{\circ}$). This material was used without purification for subsequent reactions. An attempt to remove the ether completely in order to measure the crude yield resulted in extensive decomposition.

1-Acenaphthenylmalonic acid (XVII).

Reference: Bachmann and Sheehan: J.A.C.S. 63, 204 (1941)

A solution of crude 1-bromoacenaphthene (prepared by the N-bromosuccinimide method from 6.2 gm. acenaphthene) in dry benzene (10 c.c.) was added to a chilled solution prepared from diethyl malonate (14.0 gm.), sodium (2.0 gm.) and absolute ethanol (125 c.c.). By following the procedure described by Bachmann, the crude product was isolated as a brown oil which solidified on trituration to a pale brown solid m.p. $165-168^{\circ}$ (Lit. m.p. $174.5-176^{\circ}$).

Yield = 5.15 gm. (50%)

In one experiment, the bromination was carried out on the water bath and although the yield was decreased slightly, a cleaner product was obtained.

(ii) A solution of crude 1-bromoacenaphthene (from 6.2 gm. acenaphthylene) in dry benzene (10 c.c.) was added to a chilled solution prepared from diethyl malonate (14.0 gm.), sodium (2.0 gm.) and absolute ethanol (125 c.c.). As before, Bachmann's procedure was followed and the malonic acid was obtained as an off-white solid m.p. 173-175° (Lit. m.p. 174.5-176°).

Yield = 9.20 gm. (88.1%)

Attempted Grignard Reaction with
1-Bromoacenaphthene and β -Propiolactone.

1-Bromoacenaphthene (prepared from 5.0 gm. acenaphthylene) was dissolved in dry ether (125 c.c.) and magnesium (0.8 gm.) added. The reaction was slow to begin, but once started, proceeded briskly in the cold for about one hour after which time an oily sludge began to appear on the magnesium surface. The mixture was gently boiled under reflux for a short time on the water bath but this was discontinued with the appearance of a green oil at the flask wall. The reaction mixture was allowed to stand at room temperature overnight and although the magnesium had not completely dissolved, a solution of β -propiolactone (2.4 gm.) in dry ether (50 c.c.) was added dropwise over a period of fifteen minutes, a light yellow precipitate forming.

The reaction mixture was kept below 0°C for two hours with frequent shaking and decomposed with dilute hydrochloric acid. The ethereal layer was separated and washed with aqueous sodium carbonate solution.

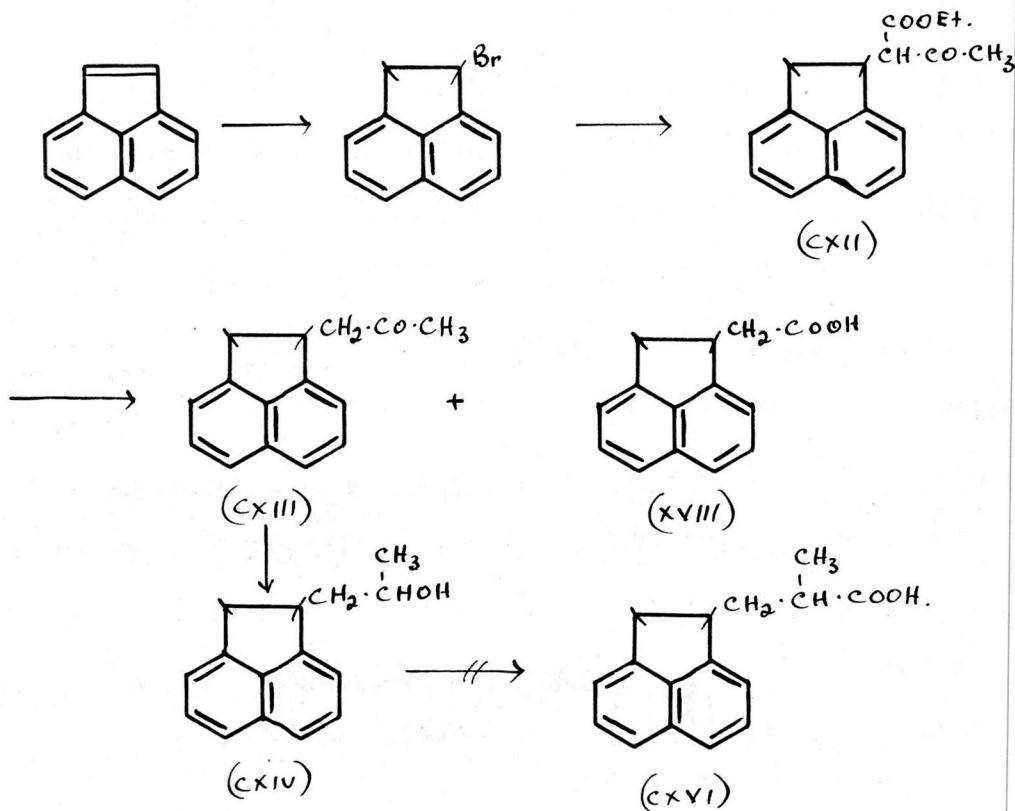
Acidification of the alkaline washings precipitated no acidic material.

The organic layer was dried (sodium sulphate) and taken to dryness. The residual black pitch was dissolved in benzene and adsorbed onto a column of alumina 16 x 3.5 cm. Two main fractions were eluted with benzene. A pale brown band was followed by a very pale yellow band showing blue fluorescence in ultra-violet light. The latter eluate on evaporation afforded a small amount of pale yellow oil which failed to crystallise. The brown band gave an amber solution showing blue fluorescence in ultra-violet light. Evaporation yielded a yellow-brown oil which on trituration with six changes of hot methanol gave a yellow solid m.p. 60-70° which did not form a picrate.

The trituration liquors were evaporated, an oily solid resulting which was taken up in benzene and adsorbed onto a column of alumina 15 x 1 cm. Development and elution with light petroleum (b.p. 60-80°) and evaporation of the various eluates resulted in a series of intractable oils.

SECTION B.EXPERIMENTAL.

(1)

An Attempted Synthesis of
2-Methyl-4:5-methylenephenanthrene.Ethyl 1-acenaphthenylacetoacetate (CXII)

Reference: Campbell, Corrigan and Campbell:
J. Org. Chem. 16, 1712 (1951)

A solution of 1-bromoacenaphthene (prepared from 50.0 gm. acenaphthylene) in dry benzene (150 c.c.) was added to a solution prepared from acetoacetic ester (91.8 gm.), sodium (16.3 gm.) and absolute ethanol (500 c.c.). The procedure described by Campbell was followed and the product obtained as a pale yellow mobile oil b.p. 169-180°/0.5 m.m. (Lit. b.p. 180-185°/2 m.m.).

Yield = 55.0 gm. (59.3%)

1-Acenaphthenylacetone (CXIII)

Ethyl 1-acenaphthenylacetoacetate (20.8 gm.) was added over a period of one hour to a simmering solution of potassium hydroxide (60 gm.) in water (280 c.c.) with stirring, alcohol (30 c.c.) being used to complete the transfer. The mixture was stirred at the boiling point for five hours before cooling and extraction with ether.

The aqueous layer on acidification deposited a pale brown solid which crystallised from cyclohexane as cream coloured plates m.p. 113-115°. A mixed melting point determination with authentic 1-acenaphthenylacetic acid (Lit. m.p. 115-116°) showed no depression.

Yield = 3.35 gm. (21.4%)

The ethereal layer was dried over sodium sulphate and the solvent removed. Distillation of the oily residue gave a yellowish oil b.p. 140-144°/0.5 m.m. (Lit. b.p. 130-135°/0.5 m.m.) which solidified on cooling to a colourless solid m.p. 40-45°. Crystallisation from light petroleum (b.p. 40-60°) afforded colourless needles of ketone m.p. 45-46° (Lit. m.p. 45.5-46.5°).

Yield = 10.8 gm. (69.7%)

1:1'-(2'-Hydroxypropyl)-acenaphthene (CXIV).

A solution of 1-acenaphthenylacetone (10.7 gm.) in dry ether (75 c.c.) was added to a briskly refluxing solution of lithium aluminium hydride (0.97 gm.) in anhydrous ether (75 c.c.) over a period of fifteen minutes. A colourless complex separated and the

mixture was boiled under reflux for three hours. The excess hydride was decomposed by the cautious addition of water and the precipitated aluminium salts dissolved in dilute sulphuric acid. The dried (sodium sulphate) ethereal layer on evaporation gave a yellowish oil which quickly solidified m.p. 63-66°. Crystallisation from light petroleum (b.p. 60-80°) gave colourless tablets m.p. 66-68°.

Analysis.

$C_{15}H_{16}O$ requires C = 84.9% H = 7.6%

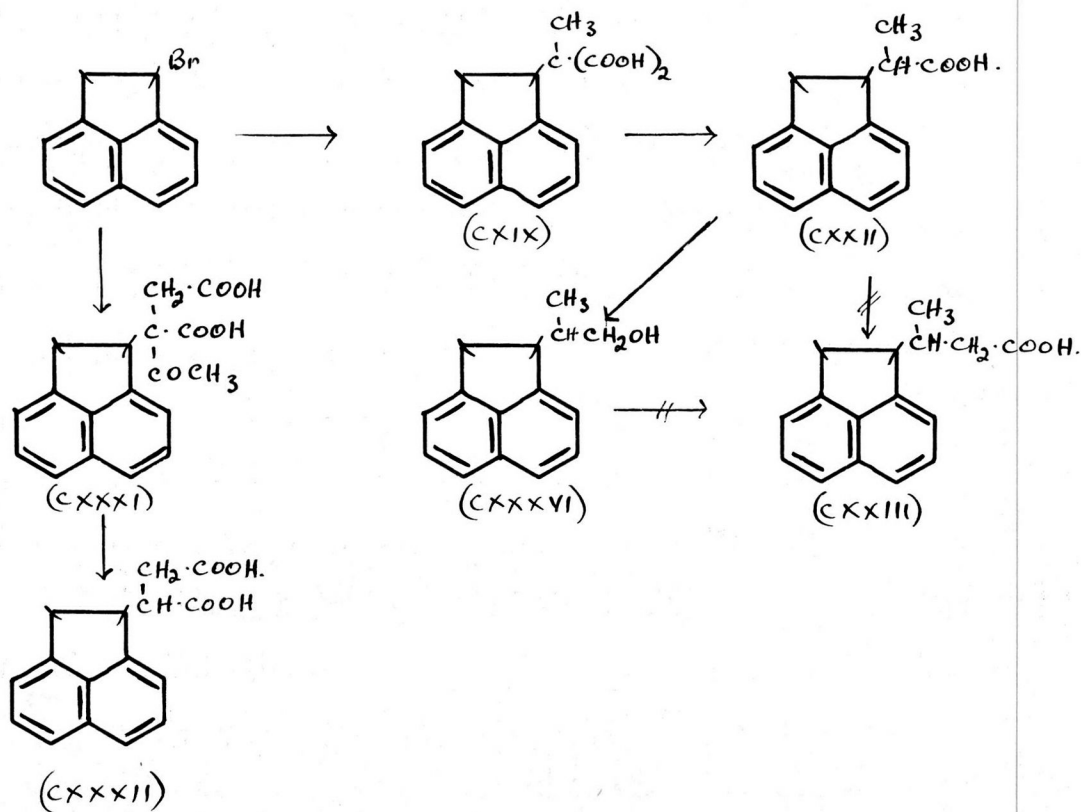
Found: C = 84.5% H = 7.8%

Yield = 9.23 gm. (85.5%)

Attempted Preparation of α -methyl- β :1-acenaphthenylpropionic acid (CXVI)

1:1'-(2'-Hydroxypropyl)-acenaphthene (1.0 gm.) in anhydrous ether (10 c.c.) was treated with phosphorus tribromide (0.17 c.c.) and the solution allowed to stand at room temperature for one hour with occasional swirling before hydrolysis with water. The ethereal layer was washed with water, sodium bicarbonate solution and again with water. Evaporation of the dried solution afforded a colourless oil which gave a positive elements test for bromine. The crude bromide was dissolved in ethanol (5 c.c.) and treated with a solution of potassium cyanide (0.46 gm.) in water (1 c.c.). The mixture was boiled under reflux for four hours, poured into water and the precipitated oil taken up in ether. The ethereal layer was dried over sodium sulphate and evaporated. The residual brown oil, which gave a

weak test for nitrogen, was boiled under reflux for twentyfour hours in a mixture of glacial acetic acid (20 c.c.), concentrated sulphuric acid (2.5 c.c.) and water (2.5 c.c.). The dark solution was cooled and poured into water and the whole extracted with ether. After washing with water, the ethereal layer was extracted with sodium carbonate solution. Acidification of the carbonate extracts gave no precipitate.

SECTION B.(ii) Attempted Syntheses of 3-Methyl-4:5-methylene-phenanthrene.Diethyl methylmalonate.

Reference: Organic Syntheses: Collective Volume II, 279.

The product was obtained as a colourless liquid
b.p. 84°/11 m.m. (Lit. b.p. 96°/16 m.m.).

Yield from 160 gm. diethyl malonate = 155 gm. (89.1%)

 α :1-Acenaphthenylpropionic acid (CXXII)

cf. Campbell, Corrigan and Campbell: J.Org.Chem. 16,
1712 (1951).

A solution of 1-bromoacenaphthene (prepared from
27.0 gm. acenaphthylene) in dry benzene (75 c.c.) was

added to a cold solution prepared from diethyl methylmalonate (62.0 gm.) sodium (8.2 gm.) and absolute ethanol (500 c.c.). A precipitate of sodium bromide appeared within a few minutes. After standing in the refrigerator for three days, the mixture was boiled under reflux for three hours and the volume reduced to 150 c.c. by distillation on the steam bath. A solution of potassium hydroxide (40 gm.) in water (40 c.c.) was slowly added and the suspension of potassium salt boiled under reflux for four hours on the water bath. Water (40 c.c.) was added and the heating continued for a further four hours. Most of the solvent was distilled off and water (100 c.c.) added. The cloudy solution was cleared by shaking with ether, separated and acidified with concentrated hydrochloric acid. A clear oil was precipitated which was extracted into ether. The dried organic layer on evaporation yielded a yellowish oil which on prolonged trituration with numerous changes of cold light petroleum (b.p. 60-80°) gave a sticky white solid. This after several crystallisations from benzene containing a little acetone afforded the malonic acid as a colourless micro-crystalline solid m.p. 109-112°.

Analysis.

$C_{16}H_{14}O_4$ requires C = 71.1% H = 5.2%

Found: C = 72.7% H = 5.3%

The malonic acid was added to the combined trituration liquors and the whole evaporated to dryness. The residual oil was heated in an oil bath at 185-190°

for two hours, although evolution of carbon dioxide appeared to stop after thirty to forty minutes. The dark residue was dissolved in acetone (300 c.c.) and boiled with charcoal for thirty minutes. Evaporation of the filtered solution gave a pale yellow oil which was dissolved in ether and extracted with aqueous sodium carbonate solution. Acidification of the carbonate extracts with concentrated hydrochloric acid gave an oil which on trituration afforded 20.35 gm. of a light brown solid.

The non-acidic ethereal solution from the decarboxylation (containing ethyl α :1-acenaphthenylpropionate) was dried over sodium sulphate and evaporated. The residue, dissolved in methanol (100 c.c.), was treated with a solution of potassium hydroxide (25 gm.) in water (25 c.c.) and the solution boiled under reflux for two hours. By conventional procedures, the hydrolysis mixture gave a further 8.95 gm. acid.

Total crude yield = 29.3 gm.
(73.0% based on acenaphthylene).

The crude acid after two crystallisations from benzene was obtained in very small colourless needles (11.6 g) m.p. 142-146°. A portion further crystallised from alcohol then from benzene-light petroleum (b.p. 60-80°) gave colourless blades m.p. 146-148°.

Analysis.

$C_{15}H_{14}O_2$ requires C = 79.6% H = 6.2%
Found: C = 79.7% H = 6.1%

The methyl ester was obtained as a colourless viscous oil b.p. 154-5°/0.7 m.m.

Analysis. $C_{16}H_{16}O_2$ requires C = 80.0% H = 6.7%

Found: C = 80.0% H = 6.7%

Yield of α :1-acenaphthenylpropionic acid = 11.6 gm.

(28.9% based on acenaphthylene)

Attempted Arndt-Eistert Reaction
on α :1-Acenaphthenylpropionic acid (CXXII).

α :1-Acenaphthenylpropionic acid (2.0 gm.) was treated with a large excess of thionyl chloride and the solution gently boiled under reflux on the water bath for two hours. Excess reagent was distilled off under reduced pressure and the last traces removed by co-distillation with 3 x 5 c.c. portions of dry benzene. The residual thick oil was dissolved in dry benzene (40 c.c.) and the solution added dropwise to a dry solution of diazomethane (prepared from 6 gm. nitrosomethylurea) in ether (200 c.c.) with constant agitation. A dark orange amorphous solid separated but only a slight evolution of gas was observed. The mixture was left at room temperature overnight and filtered. The solid was quickly added to a suspension of silver oxide (0.1 gm.) in dry methanol (100 c.c.) which had been boiled for a few minutes to form a silver mirror. No evolution of nitrogen gas was apparent, but the mixture was boiled under reflux for four hours, two further 100 mg. portions of silver oxide being added during the course of the reaction. Hot filtration gave a clear yellow filtrate to which was added a solution of potassium hydroxide (10 gm.) in water (10 c.c.) and the whole boiled under reflux for two hours. Half the solvent was distilled off and

the residue poured into water. The oily suspension which resulted was cleared by shaking with ether. The aqueous layer on acidification gave no precipitate.

The red ethereal filtrate (containing excess diazomethane and reaction products) was evaporated to dryness below 40° and the thick red oil so obtained treated as above. Acidification of the alkaline fraction of the hydrolysis mixture gave a small amount of dark oily material which was discarded.

In other experiments, where less drastic conditions were used in forming the acid chloride, no material separated from the diazomethane solution, and the reaction products consisted of dark oils which partly solidified but which could not be purified.

1:2-(1-Hydroxypropyl)-acenaphthene (CXXVI)

A solution of methyl α :1-acenaphthenylpropionate (7.0 gm.) in dry ether (50 c.c.) was added slowly to a solution of lithium aluminium hydride (2.0 gm.) in dry ether (100 c.c.). A colourless complex settled out and the mixture was boiled under reflux for three hours. Following decomposition with water and dilute sulphuric acid, the ethereal layer was dried over sodium sulphate and taken to dryness. Distillation of the residue gave a pale yellow syrup b.p. $138-140^{\circ}/0.2$ m.m.

Analysis.

$C_{15}H_{16}O$ requires C = 84.9% H = 7.6%

Found: C = 85.1% H = 7.9%

The 3:5-dinitrobenzoyl ester crystallised from a large volume of ethanol as yellow rods m.p. $123-125^{\circ}$

Analysis.

$C_{22}H_{18}N_2O_6$ requires C = 65.0% H = 4.5% N = 6.9%

Found: C = 64.9% H = 4.5% N = 6.2%

Yield = 5.45 gm. (88.1%)

Phosphorus Tribromide Treatment
of 1:2-(1-Hydroxypropyl)-acenaphthene (CXXVI).

A solution of 1:2-(1-hydroxypropyl)-acenaphthene (3.0 gm.) in dry ether (50 c.c.) was treated with phosphorus tribromide (1.0 c.c.) and the mixture allowed to stand at room temperature for one hour before the addition of water. The ethereal layer was washed with water followed by aqueous sodium bicarbonate solution. Acidification of the alkaline washings precipitated an oil which was extracted into ether and the solution dried and evaporated. The acidic residue (2.23 gm.) was dissolved in methanol (25 c.c.) a few drops of concentrated sulphuric acid added and the solution boiled under reflux for four hours. The mixture was poured into water and extracted with ether. The organic layer was washed with water and sodium carbonate solution. Acidification of the carbonate washings gave a trace of acid. The dried ethereal solution on evaporation yielded a pale yellow oil b.p. $139-140^{\circ}/0.2$ m.m. which formed a 3:5-dinitrobenzoyl ester crystallising from alcohol as yellow rods m.p. $121-124^{\circ}$. A mixed melting point determination with authentic material showed no depression.

The ethereal solution containing the non-acidic fraction from the bromination was dried over sodium

sulphate and evaporated under reduced pressure. The pale yellow syrup so obtained was shown to contain labile bromine by the alcoholic potassium hydroxide test and was used without purification for subsequent reactions. Yield = 1.92 gm. (49.3%).

Attempted Preparation of
 β :1-Acenaphthenylbutyric acid (CXXIII).

- (i) Magnesium turnings (0.12 gm.) were added to a solution of bromo compound (prepared from 1.0 gm. 1:2-(1'-hydroxypropyl)-acenaphthene) in dry ether (80 c.c.). Efforts to initiate the reaction met with no success. The mixture was gently boiled under reflux overnight, and although no apparent reaction had taken place, the clear solution was decanted from the magnesium onto crushed "cardice". When the excess carbon dioxide had evaporated, the mixture was acidified with dilute sulphuric acid and the clear ethereal layer separated. Extraction with carbonate and acidification of the washings yielded no acidic material. The ethereal layer was washed with water, dried over sodium sulphate and taken to dryness. A brown oil remained (0.57 gm.) which was shown to contain bromine.
- (ii) To a suspension of freshly cut lithium (0.11 gm.) in dry ether (10 c.c.) in an atmosphere of dry nitrogen, was added in one portion a solution of n-butyl bromide (0.81 gm.) in dry ether (20 c.c.) and the transfer completed with a little dry solvent. A brisk reaction set in which subsided after fifteen minutes and the mixture was boiled under gentle reflux for two hours,

a little dry ether being added to maintain the volume. Unreacted lithium was removed and a solution of bromo compound (prepared from 1.0 gm. hydroxypropylacenaphthene) in dry ether (25 c.c.) added dropwise to the cooled solution with constant swirling. When addition was complete, the mixture was allowed to stand at room temperature for one hour, then boiled under reflux for one hour before cooling and pouring onto crushed "cardice" (40 gm.). When the excess carbon dioxide had evaporated, dilute sulphuric acid was added and the ethereal layer washed with water followed by aqueous sodium carbonate solution. Acidification of the alkaline washings gave a cloudiness only.

Evaporation of the dried ethereal layer afforded a yellow oil (0.49 gm.) which gave a positive test for bromine.

(iii) To a solution of potassium cyanide (0.2 gm.) in water (2.5 c.c.) was added ethanol (1.5 c.c.) and the mixture added to a solution of bromo compound (0.49 gm.) in ethanol (10 c.c.). The mixture was boiled under reflux for four hours and the clear pale yellow solution poured into water (20 c.c.). The oil so precipitated was extracted into ether and the organic layer washed with water and dried over sodium sulphate. Evaporation afforded a pale yellow oil (0.46 gm.) which contained bromine but no nitrogen.

Diethyl α -acetosuccinate.

Reference: Conrad: Ann. 188, 218 (1877)

The product was obtained as a clear colourless liquid b.p. 141-145°/16 m.m.
Yield from 125 gm. ethyl acetoacetate = 130 gm. (62.6%).

1-Acenaphthenylsuccinic acid (CXXXII).

A solution of 1-bromoacenaphthene (prepared from 10 gm. acenaphthylene) in dry benzene (40 c.c.) was added to a chilled solution prepared from sodium (3.33 gm.), diethyl acetosuccinate (28.5 gm.) and absolute ethanol (80 c.c.). A light precipitate of sodium bromide appeared after a few minutes. The mixture was left in the refrigerator for three days and boiled under reflux for four hours. The volume was reduced to 100 c.c., a solution of potassium hydroxide (20 gm.) in water (20 c.c.) added and the whole boiled under reflux for two hours. Part of the solvent was distilled off and after dissolving the residual potassium salt in water, the solution was cleared by shaking with ether. Acidification gave a brown solid (4.2 gm.) which crystallised from benzene containing a little acetone m.p. 163-173°. Crystallisation from aqueous methanol (charcoal) gave a colourless microcrystalline powder m.p. 180-1°. A portion further crystallised from benzene melted at 185-6°.

Analysis.

$C_{16}H_{14}O_4$ requires C = 71.1% H = 5.2%

Found: c = 71.6% H = 5.4%

Crude yield = 4.2 gm. (23.6%)

In subsequent experiments, the crude yield was raised to 8.3 gm. (46.7%) but no pure product could be isolated. Even after nine or ten crystallisations from benzene or aqueous methanol, a product melting over the range 196-205° was obtained.

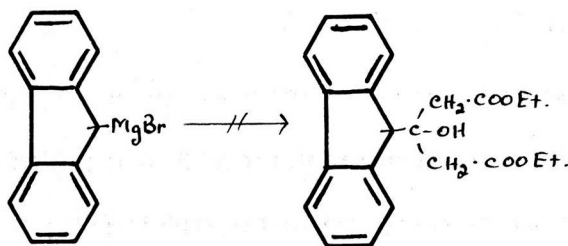
SECTION C.EXPERIMENTAL.Attempted Syntheses of 2:13-Benzfluoranthene.(a) Synthesis from fluorene.9-Bromofluorene.

Reference: Fuson and Porter: J.A.C.S. 70, 895 (1948)

Fluorene was brominated with N-bromosuccinimide in carbon tetrachloride. The product crystallised from ethanol, then from methanol, gave colourless elongated needles m.p. 102-104° (Lit. m.p. 102-104°).

Yield from 5 gm. fluorene = 3.3 gm. (46.3%)

Attempted Preparation of
Diethyl β -hydroxy- β :9-fluorenylglutarate.



(1) Magnesium (2.85 gm.) was added to a solution of 9-bromofluorene (3.1 gm.) in anhydrous ether (100 c.c.) and the mixture stirred for four hours in the cold without any apparent result. As soon as heating was commenced, a colourless crystalline precipitate began to settle out. After boiling under reflux for three hours, the suspension was decanted from the undissolved magnesium which was washed with a little anhydrous ether. The ethereal suspension was added over a period of forty minutes to a cold stirred solution of diethyl acetone-dicarboxylate (2.67 gm.) in dry ether (50 c.c.).

When addition was complete, the stirred mixture was boiled under reflux for one hour before decomposition with ice and concentrated hydrochloric acid. The deep yellow ethereal layer was filtered to remove the insoluble material m.p. 241-244°. Crystallisation from benzene gave colourless needles of difluorenyl (0.70 gm.) m.p. 246-7° (Lit. m.p. 246°).

Analysis.

Found: C = 94.3% H = 5.5%

$C_{26}H_{18}$ requires C = 94.5% H = 5.5%

The yellow ethereal layer was washed with water, aqueous sodium carbonate solution and again with water. Acidification of the carbonate washings, which had removed all the colour from the organic layer, gave no precipitate. Evaporation of the dried ethereal solution gave a crystalline residue which crystallised from benzene in colourless needles (0.35 gm.) m.p. 144-146°. A mixed melting point determination with the difluorenyl previously isolated showed no depression.

Yield of difluorenyl = 1.05 gm. (51.4%)

(ii) cf. Millar and Bachmann: J.A.C.S. 57, 766 (1935)

Ethylmagnesium bromide was prepared in the usual way from ethylbromide (10.9 gm.) and magnesium (2.45 gm.) and the ether replaced with anhydrous sulphur free xylene (50 c.c.). Fluorene (14.0 gm.) was added and the mixture boiled under reflux for sixteen hours. On cooling, the reddish supernatant liquor was pipetted off and the insoluble fluorenylmagnesium

bromide washed with 2 x 40 c.c. portions of dry xylene by stirring vigorously for a few minutes, allowing to settle and removing the upper layer as before. Anhydrous ether (50 c.c.) was added and the mixture cooled to 0° before running in quickly, with vigorous stirring, a solution of diethyl acetonedicarboxylate (6.4 gm.) in dry ether (10 c.c.). The suspension immediately thickened and was allowed to return slowly to room temperature, the buff coloured precipitate being replaced by a mobile yellow oil. After stirring for four hours, the mixture was decomposed with ice and concentrated hydrochloric acid and the deep yellow ethereal extract dried over sodium sulphate before evaporation under reduced pressure. The residual oil solidified on trituration with ethanol and after three crystallisations from this solvent gave colourless plates (1.32 g.) m.p. $114-116^{\circ}$. A mixed melting point determination with fluorene gave no depression. The filtrates were combined and boiled under reflux with 40% sodium hydroxide solution (10 c.c.) for two hours. Part of the alcohol was distilled off before pouring the cooled solution into water. Extraction with ether followed by back extraction with sodium carbonate solution and acidification afforded a negligible amount of acidic material.

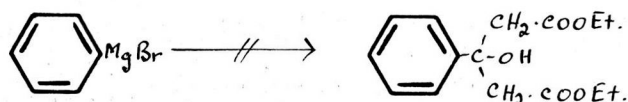
The dried ethereal layer on evaporation yielded a further 2.41 gm. fluorene (m.p. and m.m.p.).

(iii) cf. Millar and Bachmann: J.A.C.S. 57,766 (1935)

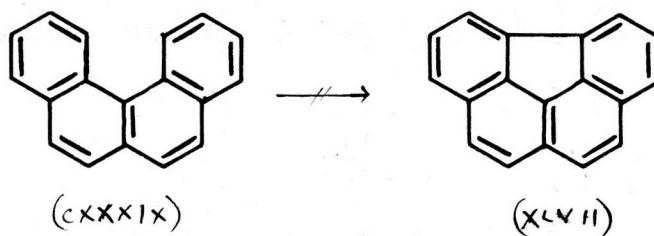
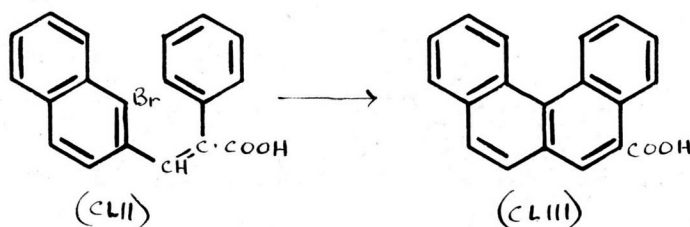
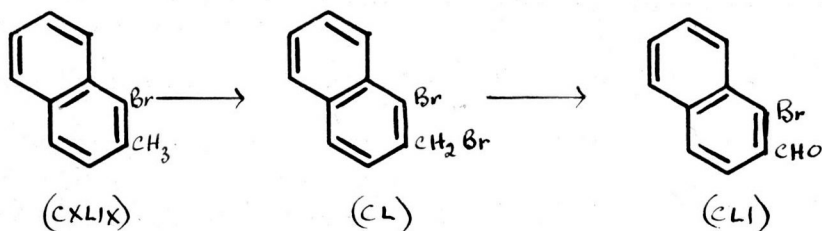
Lithium (0.76 gm.) was cut into small pieces and dropped into a flask containing dry ether (15 c.c.) and fitted with nitrogen inlet, mercury sealed stirrer and condenser. N-butyl bromide (6.85 gm.) was added all in one lot and the transfer completed with dry ether (15 c.c.). A vigorous reaction set in almost immediately and the stirred solution boiled briskly for about twenty minutes before the reaction subsided. External heating was applied and the mixture was stirred and boiled under reflux for one hour, dry ether (10 c.c.) being added to maintain the volume. The precipitate which had formed was allowed to settle and a few small pieces of unreacted lithium removed. The solvent was replaced with dry sulphur-free xylene (120 c.c.), fluorene (4.25 gm.) added and the mixture boiled under reflux on an oil bath in an atmosphere of nitrogen for eighteen hours. Most of the xylene (100 c.c.) was distilled off and replaced with an equal volume of dry ether. Diethyl acetone dicarboxylate (5.17 gm.) in dry ether (20 c.c.) was quickly run in with rapid stirring and the mixture stirred at room temperature for one hour, and boiled under reflux for a further hour before cooling and decomposition with ice and concentrated hydrochloric acid. The washed and dried ethereal extract was taken almost to dryness and a colourless solid crystallised from the residual xylene. Crystallisation

from ethanol gave 3.6 gm. fluorene (m.p. and m.m.p.) as colourless plates.

Attempted Preparation of
Diethyl β -phenyl- β -hydroxyglutarate.



To a chilled solution of phenylmagnesium bromide (prepared from 1.57 gm. bromobenzene and 0.24 gm. magnesium) in dry ether (15 c.c.) was quickly added a solution of diethyl acetonedicarboxylate (2.02 gm.) in dry ether (10 c.c.). A precipitate appeared which coagulated to a sticky gum. After stirring at room temperature for two hours, the mixture was decomposed with ice and concentrated hydrochloric acid. Evaporation of the washed and dried ethereal layer gave a little brown oil which was subjected to steam distillation. Some bromobenzene came over in the distillate and only a few particles of dark material remained in the distillation flask.

SECTION C.(b) Synthesis of 2:13-Benzfluoranthene from 3:4-Benzphenanthrene.1-Bromo-2-methylnaphthalene (CXLIX).

Reference: Adams and Binder: J.A.C.S. 63, 2773 (1941)

2-Methylnaphthalene in carbon tetrachloride was brominated in the absence of light. The product was fractionated under reduced pressure and was obtained as a pale yellow oil b.p. 171-174°/25 m.m. (Lit. b.p. 152-156°/14 m.m.).

Yield from 142 gm. 2-methylnaphthalene = 182 gm. (82%)

1-Bromo-2-bromomethylnaphthalene (CL)

Reference: Bergmann and Szmuszkowicz: J.A.C.S. 73,
5153 (1951)

1-Bromo-2-methylnaphthalene was brominated with N-bromosuccinimide. Crystallisation of the crude product from light petroleum (b.p. 60-80°) gave colourless prisms m.p. 106-108°. (Lit. m.p. = 107-108°). Yield from 88 gm. 1-bromo-2-methylnaphthalene = 91 gm. (76%)

1-Bromo-2-naphthaldehyde (CLI)

Reference: Hewett: J.A.C.S. 1940, 293.

1-Bromo-2-bromomethylnaphthalene was oxidised with hexamine in boiling glacial acetic acid. The product crystallised from the same solvent diluted at the boiling point with water as pale yellow needles m.p. 116-118°. (Lit. m.p. = 117-80°). Yield from 40 gm. 1-bromo-2-bromomethylnaphthalene = 14.8 gm. (47.3%)

 α -Phenyl- β :2-(1-bromonaphthyl)-acrylic acid (CLII)

1-Bromo-2-naphthaldehyde was condensed with sodium phenylacetate in acetic anhydride, and the crude acid purified through the ammonium salt. Crystallisation from glacial acetic acid gave off white plates m.p. 212-217° (Lit. m.p. 211-217°). Yield from 6.9 gm. 1-bromo-2-naphthaldehyde = 5.6 gm. (54%)

2-Carboxy-3:4-benzphenanthrene (CLIII)

The cyclisation of α -phenyl- β :2-(1-bromonaphthyl)-acrylic acid was effected by fusion with potassium hydroxide. The crude product was purified through the sodium salt, and the free acid crystallised from

glacial acetic acid as fine pale yellow needles m.p. 236-238° (Lit. m.p. 236-237°).

Yield from 18.3 gm. acrylic acid = 5.75 gm. (41%)

3:4-Benzphenanthrene (CXXXIX)

cf. Hewett: J.C.S. 1938, 1286.

2-Carboxy-3:4-benzphenanthrene was decarboxylated with copper-bronze in quinoline. The crude product was dissolved in benzene and adsorbed onto a column of alumina 15 x 2 cm. and developed with light petroleum (b.p. 60-80°). A single band showing blue fluorescence under ultra-violet light developed which was eluted and the solvent removed. Crystallisation of the residue from ethanol afforded colourless needles m.p. 66-68° (Lit. m.p. 68°).

The picrate crystallised from ethanol as red needles m.p. 126-8°. (Lit. m.p. 128°).

Yield from 5.5 gm. acid = 3.35 gm. (58%)

Attempted Cyclisation of 3:4-Benzphenanthrene.

Finely powdered aluminium chloride (2.0 gm.), sodium chloride (2.0 gm.) and 3:4-benzphenanthrene (0.5 gm.) were ground together and heated on an oil bath. At 130° approximately, the dark mixture began to froth, hydrochloric acid fumes being evolved. The temperature was taken to 145° and held at 145-150° for one hour. On cooling, the dark residue was triturated with dilute hydrochloric acid, filtered off and continuously extracted with benzene in a Soxhlet apparatus for one hour. The resulting solution, which was golden yellow in colour with a

green fluorescence in ordinary light and a brilliant blue fluorescence in ultra-violet light, was evaporated down to a volume of 10 c.c. and adsorbed onto a column of alumina 20 x 1½ cm. Development with light petroleum (b.p. 60-80°) produced a faint yellow band which gradually faded away as development proceeded. When a blue fluorescence under ultra-violet light began to show in the eluate, fractions were collected as follows:

- 5 c.c. Eluate colourless with faint blue fluorescence in ultra-violet light. Evaporation gave a very small amount of greenish fluorescent oil.
- 5 c.c. Eluate very pale yellow with green fluorescence in ordinary light and brilliant blue fluorescence in ultra-violet light. Evaporation gave a small amount of yellow oil with green fluorescence in ordinary light.
- 5 c.c. Eluate almost colourless with a brilliant blue fluorescence in ultra-violet light. Evaporation gave a small amount of green fluorescent oil.
- 5 c.c. Eluate colourless with a brilliant purplish-blue fluorescence in ultra-violet light. Evaporation gave a minute amount of yellow oil.
- 5 c.c. Eluate colourless with purplish-blue fluorescence in ultra-violet light. Evaporation gave no observable product.

100 c.c. Eluate colourless with purplish-blue fluorescence in ultra-violet light. Evaporation gave a very small amount of oil.

25 c.c. Eluate very pale yellow with a slight greenish fluorescence in ordinary light and a brilliant purplish-blue fluorescence under ultra-violet light. Evaporation gave a small amount of oil with a green fluorescence in ordinary light and in ultra-violet light.

50 c.c. Eluate colourless with weak fluorescence in ultra-violet light.

Evaporation gave no observable product.

Further elution of the column proved abortive. The fractions obtained above could not be crystallised and all attempts to form picrates failed. The total yield could not have exceeded 40-50 mg.

Further cyclisation experiments were carried out under the following conditions:-

(i) 4 gm. Aluminium chloride per gm. hydrocarbon. Mixture heated at 140° for one hour.

(ii) 4 gm. Aluminium chloride + 4 gm. sodium chloride per gm. hydrocarbon. Mixture heated at $165-170^{\circ}$ for ten minutes.

(iii) 4 gm. Aluminium chloride in 25 c.c. phosphorus trichloride per gm. hydrocarbon. Mixture boiled under reflux for three hours. (Bath temperature = 75°).

In all these experiments, similar results to the above were obtained.

An experiment in which the hydrocarbon (0.1 gm.) was boiled under reflux with aluminium chloride (0.2 gm.) in dry pyridine (5 c.c.) for two hours yielded unchanged 3:4-benzphenanthrene (m.p. and m.m.p.).

SUMMARY.

- (i) Various synthetic routes to 4:5-methylene-phenanthrene have been explored and although no new synthesis has been developed, Bachmann's original method has been improved.
- (ii) A shorter method of synthesising α -arylglutaric acids has been found which promises to be of general applicability.
- (iii) Attempts have been made to synthesise 2-methyl and 3-methyl-4:5-methylenepheneanthrene but without success.
- (iv) Attempts to synthesise 2:13-benzfluoranthene without the use of 4:5-methylenepheneanthrene as an intermediate were unsuccessful.
- (v) The hydrobromination of acenaphthylene as a method of preparing 1-bromoacenaphthene has been shown to be of value in synthetic work.

BIBLIOGRAPHY

1. Kruber: Ber. 67, 1000 (1934).
2. Weissgerber: Ber. 41, 2913 (1908).
3. von Braun and Rath: Ber. 61, 956 (1928)
4. Bachmann and Sheehan: J.A.C.S. 63, 204 (1941).
5. Medenwald: Ber. 86, 287 (1953).
6. Bergmann and Weizmann: J. Org.Chem. 11, 592 (1946).
7. Kruber: Private communications to this department.
8. Bachmann and Sheehan: J.A.C.S. 63, 2598 (1941).
9. Fieser and Cason: J.A.C.S. 62, 432 and 1293 (1940).
10. Campbell and Reid: J.C.S. 1952, 3281.
11. Briggs and Wilson: J.C.S. 1941, 500.
12. Koelsch: J.A.C.S. 65, 437 (1943).
13. Tucker: J.C.S. 1952, 803.
14. Ansell and Hey: J.C.S. 1950, 1683.
15. Balabon and Manchester: C.A. 41, 4517 (1947).
16. Ansell and Hey: J.C.S. 1950, 1683.
17. Bachmann and Struve: J. Org.Chem. 4, 472 (1939).
18. Papa, Schwenk and Whitman: J. Org.Chem. 7, ⁵⁸⁷,
(1942).
19. Plattner, Furst and Keller: Helv. 32, 2464 (1949).
20. Koo: J.A.C.S. 75, 1891, (1953).
21. Bruce, Sorrie and Thomson: J.C.S. 1953, 2403.
22. Barnes: J.A.C.S. 70, 145 (1948).
23. Bachmann and Sheehan: J.A.C.S. 62, 2687 (1940).
24. Schonberg and Warren: J.C.S. 1939, 1838.
25. Atkinson and Lawler: Organic Syntheses, Coll. Vol.
II, 222.

26. Bischoff and Adams: J.A.C.S. 45, 1030 (1923).
27. de Fazi: Gazz. Chim. ital. 54, 664 (1924).
28. Sircar: C.A. 27, 3930 (1933)
29. Campbell, Corrigan and Campbell: J. Org. Chem. 16,
1712 (1951).
30. Fieser and Cason: J.A.C.S. 62, 432 (1940).
31. Cogan: Bull. Soc. Chim. 8, 125 (1941).
32. McElvain and Clarke: J.A.C.S. 69, 2657 (1947).
33. Hartung and Adkins: J.A.C.S. 49, 2517 (1927).
34. Graebe and Jegquier: Ann. 290, 195 (1896).
35. Henderson: Thesis, (Edin.), 1952, 61.
36. Duthie and Plant: J.C.S. 1952, 1899.
37. Campbell and Wang: J.C.S. 1949, 1513.
38. Brown and Hammick: J.C.S. 1948, 1397.
39. Gault and Kalopossis: Compt. Rend. 229, 624 (1949).
40. Shriner: Organic Reactions, Vol. I, 4.
41. Johnston and Glen: J.A.C.S. 71, 1087 (1949).
42. Fieser and Hershberg: J.A.C.S. 59, 1028 (1937).
43. Chaikin and Brown: J.A.C.S. 71, 122 (1949).
44. Julia: Bull. Soc. Chim. 1952, 1066.
45. Fuson and Mange: J. Org. Chem. 19, 806 (1954).
46. Fuson and Frey: J. Org. Chem. 19, 810 (1954).
47. Gresham et al.: J.A.C.S. 71, 2807 (1949).
48. Cox et al.: Organic Syntheses, Coll. Vol. II, 279.
49. Blicke and Feldkamp: J.A.C.S. 66, 1087 (1944).
50. Abramov and Militskova: C.A. 46, 6082 (1952).
51. Conrad: Ann. 188, 218 (1877).

52. Swan: Thesis, (Edin.), 38.
53. Noyes and Manuel: J.A.C.S. 39, 1267 (1917).
54. Fuson and Porter: J.A.C.S. 70, 895 (1948).
55. Miller and Bachmann: J.A.C.S. 57, 766 (1936).
56. Ghigi: C.A. 40, 3110 (1946).
57. Hewett: J.C.S. 1938, 1286.
58. Adams and Binder: J.A.C.S. 63, 2773 (1941).
59. Bergmann and Szmuszkowicz: J.A.C.S. 73, 5153 (1951).
60. Hewett: J.C.S. 1940, 293.

ACKNOWLEDGMENTS.

In conclusion, sincere thanks are expressed to Dr Neil Campbell for the helpful and valuable advice he has freely given at all times. His unfailing interest and infectious enthusiasm have proved a constant source of encouragement.

Thanks are also due to Miss E.J.D. Watson, B.Sc., for assistance in the laboratory, to the University of Edinburgh for the award of a post-graduate studentship and to the Anglo-Iranian Oil Company for a grant.